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<p>(54) Title: BIAXIALLY ORIENTED POLYETHYLENE FILMS</p> <p>(57) Abstract</p> <p>Articles and films are provided from ethylene-based polymers made using a metallocene catalyst system. Biaxial orientation dramatically improves clarity, stiffness, dart drop impact, puncture resistance, and shrink. Tensile strength at yield and ultimate tensile are also improved. Film stiffness, as measured by secant modulus, is increased by 300 % over an unoriented film of the same ethylene polymer. These articles and films are useful as shrink wrap, overwrap, and for dry packaging applications such as snacks and cereals as well as non-packaging applications such as photograph and document holders.</p> <p style="text-align: right;">BEST AVAILABLE COPY</p>		

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BIAXIALLY ORIENTED POLYETHYLENE FILMS

This invention relates to a biaxially oriented film of an ethylene based polymer. More specifically, this invention relates to a film layer made from thermoplastic ethylene based homopolymer or random copolymer produced by a metallocene catalyst system, wherein the film layer is stretched in two directions for biaxial orientation.

Polymeric films are widely used, both in industrial manufacturing processes and in the non-industrial sector for the wholesale and retail delivery of goods to the consumer market. By far the greatest quantity of polymeric film, in film and bag form, is designed for, use and consumed by the non-industrial sector.

Currently, films composed of ethylene based thermoplastic polymers dominate certain of these consumer market applications -- such as the market for household disposables, trash bags and liners; overwrap films and bags for laundry and dry cleaning goods; and shipping and carryout bags for retail merchandising of non-perishable goods. In other aspects of the consumer goods delivery market, ethylene based polymer films only weakly compete, if at all, with other more expensive polymer films such as plasticized polyvinylchloride films and/or polypropylene films -- such as in the heat-shrink wrap film market for the taut-contour fit wrapping of various items, particularly perishables such as cuts of meat, poultry, and fish. Yet for other applications, such as for packaging of produce, package constructions for cereals, dry foods, and snack foods ethylene based polymer films compete somewhat in certain circumstances of these applications. At the wholesale level wherein films are used to unitize pallets and cases of goods to facilitate their shipment to a retail market current ethylene based polymer films are essentially uncompetitive with shrink-wrap and cling films of plasticized PVC or polypropylene.

Heat shrinkable films and packages thereof have gained substantial acceptance for wholesale and retail packaging of food products and goods. In the retail environment, packing films used to package food products and non-food products must be of high optical clarity (i.e., highly transparent and of low haze and, preferably high gloss) to provide an aesthetically pleasing product and must be sufficiently strong and resilient to provide the necessary protection from normal handling. Depending upon the nature of the packaged goods, the film must also possess proper barrier properties with respect to permeation by water vapor, oxygen, and/or carbon dioxide.

Successful heat shrink films and packages must satisfy a multiplicity of requirements imposed by both the packaging producer and the packaging user. Of primary importance is the capability of the film or package to physically survive intact through the process of being filled, evacuated, sealed and heat shrunk. The film package must also be strong enough to survive the

material handling involved along the distribution line to the ultimate user. In packaging foods such as meat, it is also highly desirable, even necessary, that the package film serve as a barrier to moderate and control infusion of gaseous materials (oxygen and carbon dioxide) from the surrounding environment. Of particular importance for packaging of meat products is that a film provide an effective barrier to the infusion of oxygen, since oxygen is well known to cause spoilage of meat. For bundling or unitizing non-perishable goods wherein oxygen permeation may be of less concern, the shrink wrap film must often serve a barrier function against water vapor permeation and should desirably possess a self-cling property.

Polyvinyl chloride (PVC) is now widely used for production of films used in overwrapping applications in the packaging field. PVC films are commonly used as an overwrap for trayed cuts of meat and other food products in a retail environment such as a supermarket. PVC is desirable for production of films for this service because it has excellent optics or clarity, good elasticity and strength properties at use temperatures, and satisfactory elastic memory ability and elongation. However, PVC resins have several disadvantages. PVC film has a poor resistance to physical abuse, and thus, a PVC-based film package sometimes becomes leaky during shipment. PVC film tends to tear along the edges of a sealed overwrap tray, for instance, if rubbed during transit by another tray or an enclosing carton. Furthermore, unless the PVC resin is plasticized films thereof are generally not "heat shrinkable," which means that after stretching the film while heated followed by cooling, under a later reheating an unplasticized PVC film tends not to return to its original unstretched dimension. If plasticized to enable the production of a heat shrinkable film, then significant concern has to be given to the nature of the plasticizer used, its quantity and compatibility with the PVC resin and migration of such plasticizer from a film thereof and its suitability for contact with foodstuffs.

The packaging industry, particularly for perishable food products and individually wrapped non-food items, desires a film having the advantages of PVC, but without the disadvantages described above. For such applications the film should be of high clarity, tear resistant, puncture resistant, and the film should exhibit resistance to deformation or good recovery from deformation and satisfy food law requirements.

The use of films of vinylidene chloride-vinyl chloride copolymer, introduced under the trademark Saran, is presently popular due to the physical characteristics of a film produced from such resin. It is clear, has a high tensile strength, forms a good barrier against moisture and vapor transmission, is mildew resistant, has good conformability to the item being wrapped, may be formulated for high slip, and it possesses an inherent self-adherability or "cling."

Vinylidene chloride-vinyl chloride copolymer films are typically formed by extruding the resin in the form of a blown tube which is then super cooled. This process of forming the initial film layer may cause a certain degree of orientation to occur in the film layer but (due to the relaxation properties of this resin) such residual orientation as may remain in the film layer due to its bubble extrusion forming is not typical of the morphology that subsequent stretching of the film layer in a machine direction (MD) induces. Such vinylidene chloride-vinyl chloride copolymer blown films may be subsequently oriented by stretching in a longitudinal or machine direction as a second bubble while the so produced film layer is still warm and soft after which it is cooled.

Unfortunately, a vinylidene chloride-vinyl chloride copolymer oriented film does not respond well to later applications of heat. Heat causes instantaneous film shrinkage because orientation is lost, heat seals with such films are not smooth, resulting in a weak seal. Furthermore, hot melt coatings of this oriented film with another polymeric material to produce a film composite or multilayer film having more desirable characteristics is not possible. The oriented film loses its orientation upon contact with a hot melt. In lamination, the hot press rolls usually cause the oriented film to react similarly.

Characteristics such as heat sealability are not the only criteria by which one evaluates a film structure for suitability to shrink wrap products such as compact discs, pallets of individually wrapped items, or the like. Strength and clarity are very important characteristics in such packaging. To obtain these desirable shrink characteristics, conventional shrink bags are today constructed of ethylene vinyl-acetate copolymers. These copolymers often have a vinylidene chloride - vinyl chloride or ethylene vinyl alcohol copolymer layer serving as a water vapor barrier. However, films from these resins tend to be soft and cloudy, rendering the film unsuitable with respect to appearance and vulnerable to failure at conditions of operation due to the relatively high temperatures to which it is exposed in the orientation and shrinking process.

By reason of their lower cost, ethylene homopolymers and copolymer resins and blends thereof enjoy widespread use in the packaging industry for certain applications. Typically, polyethylene (PE) resins employed as such or as a blend component in packaging are high density (HDPE), linear low density (LLDPE), low density (LDPE), very low density (VLDPE) or ultra low density (ULDPE). LLDPE, VLDPE and ULDPE are ethylene copolymer wherein, typically, the comonomer is a C_3 - C_{20} alpha-olefin. The comonomer introduces branching into the polymer and affects its density. These polyethylenes have been and still are typically made with traditional Ziegler-type catalysts which contain different types of reaction sites resulting in a polyethylene resin containing a broad range of molecules. For instance, such polyethylene typically contains polymers

having a medium molecular weight with medium branching fraction, a low molecular weight and high branching fraction, and high molecular weight with low branching fraction. This results in inconsistent properties, and sometimes, poor clarity when such resins are converted into films as well as certain difficulties in production of the film itself.

Today, many oriented polymeric films are of multiple layer construction and comprised of at least one barrier or oxygen layer, such as ethylene polyvinyl alcohol (EVOH) or vinylidene chloride-vinyl chloride copolymer, and a of different polyethylenes or of polyethylene layer such as LLDPE, HDPE, LDPE, VLDPE, or blends of polyethylene with acetates, such as ethylene-vinyl-acetate (EVA). This is because EVAs having greater than about 85 wt % ethylene provide substantial structural strength to a film during the second bubble orientation process, and are especially beneficial for the orientation of tubular films. Such multiple layer films are formed by a number of ways, including coextrusion, lamination and coating techniques.

A heat shrinkable film should be susceptible to orientation without distortion or separation of the multiple layers which are typically present in films of this nature. The film layer must be strong enough, at the orientation temperature, to withstand the stretching in either of the machine direction (MD) or transverse direction (TD) without the creation of holes, tears, or non-uniform zones of stretching. In the case of blown tubular film, the film layer must be capable of supporting the stretching bubble during the orientation process. With multi-layer film constructions, each layer of the film should be susceptible to orientation without fracture, separation, or creation of holes in the layer. In packaging use, the final film product should respond to heat rapidly enough for commercial practicality, and yet must not exhibit such a level of shrink energy as would cause the multiple layer film to pull apart or de-laminate during shrinkage under its own internal forces.

Preferably, oriented films used for shrink packaging should be clear enough for a consumer to visually inspect the packaged item prior to purchasing. If the packaging is cloudy (hazy) or not sufficiently transparent or translucent, a wrapped food item will appear to be undesirable to the consumer. Thus, clarity is a product attribute widely sought in many types of polymer films for certain application.

In the past, thermoplastic ethylene based polymers have not been adopted by the industry for applications that require softness, but with good shape retention or recovery (snapback). Polyethylene films, particularly those of a LDPE or LLDPE, have traditionally been relatively soft or limp, having a low secant modulus, and softness is a desirable property in some applications, such as for wrapping a meat product. This would appear to make polyethylene resins desirable for production of films for such services, which due to its lower density and cost, would desirably

displace PVC films from these services. However, polyethylenes have been largely unsuccessful in replacing PVC in at least the meat wrap application, primarily because a polyethylene film retains or recovers its shape poorly after handling, leaving unacceptable fingerprints on the film. PVC films, on the other hand, snaps back or recovers its shape a few minutes after handling, providing a fresh appearance.

In yet other applications, such as in packaging snack foods, such as potato chips, a film should feel stiff to protect and/or convey the crisp and crunchy nature of the product. The softness of an ethylene based polymer film has rendered it undesirable for this service. Today the film widely employed for snack food packaging is biaxially oriented polypropylene (BOPP) film due to its high degree of stiffness, its good optical properties of low haze and high gloss, and good barrier properties to water vapor transmission.

For fresh-cut produce, today modified atmosphere packages are desired. A modified atmosphere package (MAP) is one wherein the film material of its construction has breathing characteristics within specifically intended ranges relative to the transmissibility of the film to oxygen, carbon dioxide and water vapor. In a modified atmosphere package the transmissibility of a film to these vapors must neither be too low nor too high but should instead correspond to the "respiration" of the produce product for these vapors. For example, a film for MAP applications should have an oxygen transmission rate (OTR) of about 300-1200 cc mil/100 in² atm/day, a carbon dioxide transmission rate (CO₂TR) of about 1,000 to 5,000 cc mil/100 in² atm/day and, to prevent dry rot of produce, a water vapor transmission rate (WVTR) of less than 2.5 g mil/100 in² day. Resins widely used today for MAP applications are Ziegler catalyst produced VLDPE films despite their limited OTR and poor haze properties and EVA films despite their poorer WVTR properties.

Because an ethylene based polymer is generally a lower cost product, it has long been seen as a desirable goal to use a thermoplastic polyethylene for various uses that have been heretofore dominated by higher cost polymers. However, ethylene-based polymers heretofore available have lacked various properties required for a particular film service or were otherwise objectionable. For some applications, such as snack food packaging, polyethylene was considered too soft and lacking in stiffness. As a shrink wrap film, it has heretofore been necessary to form such films from the heretofore available polyethylene resins by a blown bubble extrusion process and then orient it by a double bubble procedure. Formation of a biaxially oriented film of polyethylene by a slot-die casting tenter frame stretching process in which the degree of orientation may be more varied and precisely controlled has not been practical due to the tackiness and inadequate melt strength and

excessive melt elasticity of a film layer of an ethylene polymer at the conditions required for tenter frame stretching.

Cast and blown bubble films prepared from the same ethylene polymer resin and to the same gauge differ dramatically with respect to their haze and gloss properties. Cast films have significantly lower haze and significantly higher gloss than do blown bubble films of the same ethylene polymer resin. In either case, cast or blown bubble films, as the density of the ethylene polymer resin of which the film is formed increases the haze of the film increases while its gloss decreases; with the rate of increase/decrease of haze/gloss with increasing resin density being significantly greater for blown bubble than for cast films.

In some cases, wherein good film optics are requisites for use of a film, low haze/high gloss properties may be obtained in a cast film of a low density ($d < 0.940 \text{ g/cm}^3$) ethylene polymer (LDPE or LLDPE); but such LDPE or LLDPE films are attended with a lower set of physical strength properties (tensile, elongation, tear resistance) than could be attained with a high density ($d \geq 0.940 \text{ g/cm}^3$) ethylene polymer (HDPE). Even then, such good optics cannot be attained with such low density ethylene polymers in a blown bubble film. On the other hand, wherein the physical strength properties required of a film exceeds those that can be obtained with a low density ethylene polymer, a high density ethylene polymer can be employed for the cast or blown bubble extrusion of a film to attain the requisite film strength properties but at a sacrifice of the film optics, with this sacrifice being much greater for blown bubble films.

Today such ethylene based polymer films that have been proposed as biaxially oriented heat shrinkable films are those prepared from a blend of a low density ethylene polymer of density from about 0.91 to 0.93 g/cm^3 and a high density ethylene polymer of density from about 0.940 to 0.98 g/cm^3 , as described for example in GB 937,807 and GB 1,279,714, or a low density ethylene polymer and a very low density ethylene polymer of density from about 0.87 to 0.910 g/cm^3 , as described for example in EP 0299750 and U.S. Patent 4,801,652. Even then such ethylene based polymer blend films have not been widely adopted for certain services such as food packaging because of certain real or perceived deficiencies in their properties and/or difficulties in their production.

Film producers and converters recognize that there is a need for a polyethylene (ethylene homopolymer and/or ethylene copolymer) that can be fabricated to a film form of high clarity and high stiffness and/or high clarity and good snapback. Further, a film produced from any polyethylene should have good impact and puncture resistance, increased tensile at yield and other physical properties, and low levels of extractables so as to not impart unpleasant odors or tastes to

a food product. Proper shrink properties are also desired for certain applications such as packaging certain food products and goods, covering windows, and wrapping meat pallets.

A film should have as few layers as possible, but with a desirable combination of properties. There is a need for a one-, two- or three- layer film structure that may be produced from a thermoplastic ethylene based polymer resin that has good clarity, high strength, and which can be readily heat sealed with a strong seal resulting and printed upon with protection for the printing, which may be biaxially oriented to yield a heat shrinkable film.

It has now been found that ethylene based polymers produced from a catalyst having essentially only one type of catalytic site may be fabricated into oriented films having improved properties with respect to heat sealability, greater impact strength, puncture resistance, and optimal optic properties such as haze and gloss. It has further been found that an ethylene based thermoplastic polymer produced with a metallocene catalyst may be fabricated into a film which can meet the needs of the food packaging industry, the pallet shrink-wrap industry, and the market for individual shrink wrapped goods.

This invention comprises a film layer formed by cast or blown bubble extrusion of a single ethylene polymer resin which is then biaxially oriented by a tenter frame or double bubble procedure to yield a biaxially oriented film layer that has good optical properties of low haze and high gloss -- like that of a cast extrusion LDPE film -- while exhibiting high strength properties -- like that of a cast or blown bubble extrusion HDPE film.

It has been found that certain ethylene homopolymers and copolymers (ethylene based polymers) made utilizing metallocene catalysts, after being made into a film and subsequently oriented in at least two directions show a surprising ability to withstand such orientation, as well as displaying enhancements in important physical properties after such orientation, when compared to other previously known ethylene polymers in general, and linear low density polyethylenes (LLDPE) in particular, most especially those polyethylenes made using traditional Ziegler-Natta catalysts. In one embodiment of the present invention, the most striking improvements are evidenced in clarity (manifested in haze and gloss), dart drop impact resistance, puncture resistance, oxygen and water vapor transmission rates, tensile at yield, secant modulus, and the like.

In an embodiment of the present invention, extruded articles such as film, or other fabricated articles made from such film, are comprised of an ethylene homopolymer or a copolymer of ethylene and at least one C₃-C₂₀ alpha-olefin. The alpha-olefin of the copolymer is present in the range of from about 0.01 to about 6.0 mole percent of the copolymer, for C₄-C₂₀ alpha-olefins preferably no greater than 5.0 mole %. The ethylene based polymer will have a content of ethylene greater than

90 wt%, a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) of $M_w/M_n \leq 3$, a ratio of a Z - average molecular weight (M_z) to weight average molecular weight of $M_z/M_w \leq 2$, a composition breadth distribution index (CDBI) of 50% or preferably greater, such as 55 %, a density in the range of from about 0.915 to about 0.965 g/cm³, an I_{21}/I_2 melt index ratio (MIR) of less than about 22, a Dow Rheological Index (DRI) of < 0.3 , and a peak melting point (DSC) from about 103-135°C.

Biaxially oriented film made from such ethylene based polymers will exhibit certain film properties that are relatively sensitive to a change of polymer density, such as

- (a) Secant Modulus (MD/TD), which increases with increasing density;
- (b) Tensile Strength at Yield, which increases with increasing density;
- (c) Elongation at Break, which decreases with increasing density;
- (d) Oxygen Transmission Rate (OTR);
- (e) Water Vapor Transmission Rate (WVTR);

film properties that are relatively sensitive to resin density changes from about 0.915 to about 0.930 g/cm³ and thereafter relatively insensitive to density changes beyond 0.930 g/cm³, such as

- (f) Tensile strength at Break;
- (g) Elmendorf Tear;
- (h) Puncture Strength;
- (i) Dart Impact Strength, which is greatest at the 0.917 to 0.922 g/cm³ density range, and declines significantly by comparison as density increases beyond 0.922 g/cm³;

and film properties that are somewhat insensitive to a change in polymer density, such as

- (j) Haze;
- (k) Gloss;
- (l) Shrinkage.

Further, with an ethylene based polymer of an appropriately selected density, a film may be engineered to provide a target or desired property value relating to film strength, vapor barrier properties and the like by appropriately controlling the conditions and degree of orientation imparted to it in the MD and TD.

In certain embodiments of the invention a biaxially oriented film comprised of such ethylene based polymers will exhibit properties such as:

- a) haze in the range of from 0 to 5%;
- b) gloss above about 65%;

- c) dart drop impact above 400 g/mil at a resin density of 0.917 g/cm^3 and no lower than 150 at a resin density of 0.940 g/cm^3 ;
- d) oxygen transmission rate below about 600 cc-mil/100 in²-atm/24 hours @ 25°C;
- e) a tensile at yield of 2000 psi or greater (MD) or 5000 psi or greater (TD);
- f) a secant modulus (1%) above about 40,000 psi (MD), or above about 70,000 psi (TD) and;
- g) shrinkage of at least 10% in each of the oriented directions.

Those of ordinary skill in the art will understand that for a given polymer at a given temperature, the more highly oriented film will shrink more than a film of lower orientation (at same temperature and base polymer density). Shrinkage will occur at a temperature range of 70° to 90°C within 10 seconds, preferably the shrinkage occurs in a temperature range of 75 to 85° within 5 seconds.

Shrink films made from such ethylene homopolymers and ethylene-alpha-olefin copolymers and articles made from these films will be particularly useful in applications where maximizing optical properties, secant modulus, impact resistance, puncture resistance and the like are important.

Thus, one preferred embodiment of the present invention provides an ethylene based polymer film having an oxygen permeability no greater than about 500 and typically about 150-450 cc/100 in²/24hr. The film comprises a biaxially oriented (BO) film having increased optical clarity, puncture resistance and tensile strength, said film comprising at least one layer of an ethylene copolymer thermoplastic resin produced from a metallocene catalyst and having an ethylene content of greater than 90 wt%, a density range from 0.915 g/cm^3 to about 0.930 g/cm^3 . The film layer is biaxially orientable to an extent of 5 x 8 or 7 x 7 (MD x TD). The biaxially oriented film (BOF) is heat shrinkable and more preferably exhibits a 76% shrink in the machine direction. In addition, the film is 100% recyclable.

Another preferred embodiment of the present invention also provides a biaxially oriented (BO) film comprising at least one layer of linear low density ethylene-alpha-olefin copolymer density of 0.915 to 0.940 g/cm^3 polymerized with a metallocene catalyst, which may hereafter be referred to as a "m-LLDPE" resin. The m-LLDPE film has improved optical clarity and physical toughness for biaxial orientation, and optionally may comprise a second and third layer. In a preferred embodiment, the BO-m-LLDPE-film includes a first layer and a second layer that are co-extruded. The BO-m-LLDPE-film can also include a fourth layer adhesively laminated to the third layer.

The present invention also comprehends packages fabricated from the films of the invention wherein the second or third layer is heat sealed. The invention further includes a method for

packaging a product such as a compact disc or software package and shrink wrapping the product in a package made from the BO-m-LLPDE-film of the present invention. In addition, the invention comprehends a method for wrapping an item, preferably a window frame or door frame comprised of the film of the present invention.

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings.

A radar plot or diagram is a multiple axis (≥ 3) graphs wherein each radiating axis from the center point of its origin to its end point represents a range of values -- either actual or as a percentage of an assigned maximum value (relative) -- with each axis representing the value range of a different chemical/mechanical/physical property of the final film product or the film resin, as may be indicated on the plot. In this respect the differences and/or similarities between one film and another, or the relationship between a change in resin property to a change in a final film property (actual or relative) may readily be viewed and assessed.

Fig. 1 is a radar plot by which the final film properties of an m-E-polymer BO film of 1.62 mil thickness and 5 x 8 orientation of this invention is compared on a relative basis to a blown but unoriented m-E-polymer film prepared from the same resin, namely EXCEED 350 D60.

Fig. 2 is a radar plot by which the final film properties of an m-E-polymer (EXCEED 350 D60) BO film of 1.62 mil thickness and 5 x 8 orientation of this invention is compared on a relative basis to a commercially available film of biaxially oriented polypropylene (BICOR®B, from Mobil Chemical Co.).

Fig. 3 is a radar plot by which on a relative basis the final film properties of an m-E-polymer (EXCEED 301) BO film of 5 x 5 orientation of this invention is compared to a blown film of a high density polyethylene.

Fig. 4 is a radar plot by which on a relative basis the final film properties of three BO films of EXCEED resins of different densities (0.917; 0.922; 0.926-g/cm³) are compared; the 0.917 g/cm³ density resin BO film (350 D60) being of 5 x 8 BO and 1.62 mil gauge and the other films being of 6 x 6 BO and 0.6 mil gauge.

The present invention comprises the utilization of ethylene based polymers having certain minimum characteristics with respect to their ethylene content; molecular weight, both M_w and M_n ; their density; and the compositional uniformity of the ethylene based polymer resin: for the production of a film layer which upon biaxial orientation yields a film article having a set of physical/mechanical/chemical properties requisite to the service required of such film for various

particular applications which heretofore have not been particularly serviceable by an ethylene based polymer film.

The present invention concerns certain classes of biaxially oriented films fabricated from ethylene based polymers made utilizing a metallocene catalyst system, articles made from these films, and uses of the films and/or articles. For purposes of this application, such ethylene based polymers include ethylene homopolymers and ethylene copolymers in which ethylene is the predominate monomeric constituent by weight or mole %; specifically, ethylene comprises at least and preferably more than 90 wt % of the ethylene based polymer while the comonomer content thereof does not exceed 6.0 mole % of the ethylene based polymer and the CDBI of the polymer exceeds 50%. Preferably such ethylene based polymers comprise at least about 93 wt % ethylene monomeric units and the comonomer content thereof does not exceed 5.0 mole % and more preferably the comonomer content does not exceed about 3.3 mole % of the ethylene based polymer. Such ethylene based polymers may hereafter be referred to generally as an "m-polyethylene" or as an "m-E-polymer."

The term "oriented" means that the m-E-polymer film has been stretched while in a softened state while at a temperature below that at which the film layer was initially extruded by a cast or blown bubble technique, and "biaxially" means that the cast or blown bubble m-E-polymer film has been stretched in both of a machine direction (MD) and a direction transverse to the machine direction (TD), as described further below. The degree of biaxial orientation is denoted as the percentage as compared to the original dimensions of the extrusion formed film layer that the film layer is stretched; i.e., such as 100, 200...600 % of its original dimension of length (MD) or width (TD). For example 1x1 orientation means that the initial film layer has been stretched to twice its original dimension in each of the machine direction (MD-length) and transverse direction (TD-width); 6x6 would denote a stretching to six times the original length and width dimensions of the initially formed film layer. Films produced of the particular ethylene based polymer in their biaxially oriented form have unique characteristics, which may be manipulated by the degree of or type of orientation, which make them well suited for use in certain service applications.

The term ethylene copolymer as used herein shall mean copolymers of ethylene and alpha-olefins. Such alpha-olefins will generally have 3 to 20 carbon atoms. Polymers of ethylene and one or more of these alpha-olefins are contemplated. Preferred alpha-olefins are butene-1, pentene-1, 4-methyl-1-pentene, hexene-1, octene-1 and decene-1. Especially preferred are butene-1, hexene-1, and octene-1.

Compared to films made from previously available ethylene homo and alpha-olefin copolymer, the present invention provides an m-E-polymer film layer that is biaxially orientable without difficulty by either of the double bubble or tenter frame processes to yield an oriented film having superior optical properties, outstanding dart drop impact resistance and puncture resistance, and a dramatically increased secant modulus. A biaxially oriented m-E-polymer film according to the present invention is a stiffer film than previously available polyethylene films, has improved clarity, and is better able to withstand the rigors that a film encounters in service. Consequently, articles made from these biaxially oriented m-E-polymer films (BO-m-E-polymer films) exhibit superior properties, which allows the ethylene based polymer films of the present invention to be designed for and used in applications for which polyethylene was previously considered unattractive.

The present invention provides various articles of manufacture, typically for packaging, and methods for making these articles. Articles contemplated by the present invention include a shrink wrap pallet film; a film for wrapping goods, packages for goods such as snacks, including potato chips and dry cereals; shrink wrap films for meats and poultry; and typical film applications such as diaper backsheet. Depending upon the film stiffness required for a particular end use application, the required stiffness (secant modulus) may be engineered into the final film product, ranging from relatively soft to relatively stiff, by control of the degree of orientation imparted to the film in one or the other, or both, of the MD and TD. The present invention provides BO-m-E-polymer films for shrink wrapping individually packaged items, with applications ranging from packaging compact discs to providing poultry bags. Some of the BO-m-E-polymer films embodying this invention are serviceable as heat shrinkable packages in which a product is inserted, air is normally evacuated, the open end of the bag is closed, such as by heat sealing, and heat is applied to shrink the film for a tight and conforming fit around the product.

In other service applications wherein heat shrinkability of a film is either not desired or is an inconsequential property that will not be employed in the use of the film -- services such as liners for cereal box packaging, snack food packaging, overwrapping of fresh cut produce, and the like -- by appropriate selection of m-E-polymer resin density and control of the degree of orientation imparted to the film, final film products of a desired degree of stiffness and of a desired range of vapor transmissibility to O₂, CO₂ and H₂O may be produced that are structurally strong (tensile strengths, puncture strengths, tear strengths) and of good optical properties (haze and gloss).

The end use service intended for the m-E-polymer film will in part influence the selection of the ethylene polymer resin for production of the film layer and thereafter the conditions employed

for its orientation in the MD and TD. For example, films may be intended for service as a general heat shrink wrap for non-perishable good or for perishable food goods such as meats, or the like. The intended service will then require as final properties of the film certain minimum properties with respect to (1) haze and gloss, depending upon whether user viewability of the packaged goods are or are not of a practical concern; (2) oxygen and moisture barrier moderating properties, a particular concern with respect to food packaging; (3) secant modulus (flexibility - resistance to deformation), to be geared to the preference of the end user market; (4) degree of shrinkability, to be geared to the preference of the end user market; (5) puncture resistance, tensile impact, tear strengths and elongation properties of suitable minimums for service. The requisite minimum service properties required of the film for use in a particular application is then imparted to the film by proper selection of the film base m-E-polymer resin and the selection of the film forming and orientation conditions.

The m-E-Polymer Resins

Catalyst for polymerization of the ethylene based polymers here concerned are comprised of a transition metal component having at least one organo ligand which contains a cyclopentadienyl anion moiety through which the organo ligand bondingly coordinates to the transition metal cation. Such catalyst systems are now commonly referred to as "metallocene" (m) catalysts and many examples of such metallocene catalyst systems have now been described in the art.

In contrast to catalyst systems theretofore known for alpha-olefin polymerization that utilize a transitional metal component not having an organo ligand having a cyclopentadienyl anion moiety, now commonly referred to as conventional or traditional Ziegler-Natta (ZN) catalysts, metallocene catalysts are essentially single cited catalysts whereas ZN catalysts are multi-sited catalysts that generally produce a polymer resin having a great diversity of polymeric species. By contrast, an ethylene-alpha-olefin copolymer produced by a metallocene catalyst is generally much more uniform with respect to the polymeric species that comprise the resulting m-E-polymer resin, particularly with respect to the disparity between the differing molecular weight fractions thereof -- as indicated by the M_w/M_n value of the m-E-polymer resins generally being ≤ 3.0 -- and with respect to the distribution of alpha-olefin comonomer between the different molecular weight fraction thereof -- as indicated by a high comonomer distribution breadth index (CDBI) value of 50% and higher. In part, by reason of the greater compositional and molecule weight distribution uniformity achieved in an ethylene based polymer produced by a metallocene catalyst, the density of the resulting m-E-polymer resins is substantially a linear function of its mole % comonomer content and densities of the m-E-polymer resin in the 0.915 to 0.965 g/cc range of interest for films of this invention may be accomplished with an ethylene content of greater than 90 wt % and a comonomer

content not exceeding about 6.0 mole %, and a comonomer content preferably not exceeding about 5.0 mole %, and more preferably of or less than 3.3 mole %. Further, such densities are achieved in the m-E-polymer resin while the polymer backbone remains substantially linear; that is, such short chain branching (SCB) that occurs along the polymer backbone is due substantially only to the alpha-olefin comonomer content of the polymer. Accordingly, although the final density of the ethylene copolymer varies somewhat depending upon the carbon number of the comonomer utilized, the magnitude of this variation with C₄-C₂₀ alpha-olefin comonomers is not substantial; the requisite copolymer densities required of the m-E-polymer resin for films of this invention may readily be achieved with low contents of comonomer such as the C₃-C₈ alpha-olefins, with butene-1 and hexene-1 preferred as the comonomer by reason of their lower cost. Such m-E-polymers having these requisites have recently become commercially available from Exxon Chemical Company in Baytown, Texas and are now identified by the trademark "EXCEED."

Production of the m-E-Polymer Resins

The ethylene based polymers utilized in the present invention are preferably produced using supported or unsupported metallocene catalysts. The polymers may be produced in many types of reactors or reaction schemes, including, but not limited to, fluidized bed or stirred bed gas phase reactors, slurry or bulk liquid reactors of tank or loop type, solution, or any other process practiced for the polymerization or copolymerization of ethylene.

Specific metallocene-type catalysts are known to be useful for producing olefin polymers, and such catalysts are described in U.S. Patent No. 5,324,800. For placing catalyst systems on a supporting medium and using the resulting catalyst, see, for example, U.S. Patent No. 5,124,418. Support techniques for metallocene-type catalysts for use in the preparation of alpha-olefin polymers are described in U.S. patent 5,240,894. While catalysts used for the examples which follow were employed in a gas phase fluidized bed polymerization, catalysts for commercial use may be used in other processes including for example, slurry and solution processes. U.S. Patent Numbers 5,324,800; 5,124,418; and 5,240,894 are hereby incorporated by reference for purposes of U.S. patent practice.

In one preferred embodiment, a catalyst system comprising bis(1,3 methyl-n-butyl cyclopentadienyl)zirconium dichloride activated with methyl alumoxane (MAO) is the catalyst of choice. Such catalysts are outlined in copending U.S. Application Serial Number 08/466,587 which is included herein by reference for purposes of U.S. patent practice.

Characteristics of the m-E-Polymer Resins

The ethylene polymers of the present invention will generally have a narrow molecular weight distribution (MWD), as characterized by the ratio of weight average molecular weight (M_w) to number average molecular number (M_n), M_w/M_n . These M_w and M_n values are determined by Gel Permeation Chromatography (GPC). The MWD for the m-E-polymers of the present invention is less than or equal to 5; preferably ≤ 3.5 , more preferably ≤ 3.0 ; and most preferred ≤ 2.5 . Embodiments of these m-E-polymers will have a density in the range of from about 0.915-0.965, preferably 0.917-0.95, more preferably 0.917-0.940 and most preferably from 0.920 to 0.94 g/cc.

Resins produced by the above referenced processes and catalysts will be homopolymers or copolymers that contain greater than 90 wt % ethylene, preferably 93 wt % ethylene or greater, and may incorporate one or more alpha-olefins comonomers in the range of from about 0.01 mole percent to about 6.0 mole %, preferably 5.0 mole % or less, and most preferably no more than about 3.3 mole % comonomer. In a preferred embodiment, the comonomer ranges from about 0.1 to about 3 mole percent.

Copolymers produced from a catalyst system having a single metallocene component have a very narrow composition distribution - most of the polymer molecules will have roughly the same or comparable comonomer mole % content. Ziegler-Natta catalysts, on the other hand generally yield copolymers having considerably broader composition distribution meaning that comonomer inclusion varies widely among the polymer molecules.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI") as defined in U.S. Patent 5,382,630 which is hereby incorporated by reference. CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature all fractions are assumed to have an $M_n \geq 15,000$, where M_n is the number average molecular weight of the fraction.

Low weight fractions generally represent a trivial portion of the polymer. The remainder of this description and the appended claims maintain this convention of assuming all fractions have $M_n \geq 15,000$ in the CDBI measurement.

From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has a comonomer content within 25 % of each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993. The m-E-polymers employed in the films of this invention have CDBI's equal to or greater than 50% the range of 50-98%, usually in the range of 50-70% and most typically in the range of 55-60%.

These m-E-polymer resins have a melt index (MI) in the range of from about 0.5 to about 10, preferably in the range of from about 1.0 to 5.0, and more preferably from 1 to 4.0 dg/min. The MI range for film production of an m-E-polymer via a blown tube technique is preferably from about 0.8 to about 2.0; for cast film production the MI range of the m-E-polymer is preferably from about 0.75 to 4.0; preferably 1 to 5.0; more preferably 1 to 4. Choice of melt index for the m-E-polymer will generally be driven by the type of extrusion process and the specific equipment in use as well as the end use for films and/or subsequent use in converting operations.

Food law compliance can be an important criterion for articles made from these resins, such compliance is usually directly affected by the extractable content of an article made from a resin. Using an n-hexane reflux procedure, a standard of the U.S. Food and Drug Administration as noted in 21 C.F.R. § 177.1520, the maximum extractables level of the products of the present invention is expected to be less than about 5 wt%, preferably less than about 4 wt%, and most preferably less than about 3 wt%.

The m-E-polymers used in this invention have an I_{21}/I_2 or melt index ratio (MIR) less than 35, generally in the range of from about 16 to 22. DRI ranges from about 0 to 0.4, preferably from about 0 to 0.25, more preferably from 0 to 0.2, and most preferably from about 0 to 0.15. A definition of DRI and test methods for it are described in the publication ANTEC '93 Proceedings, INSITE™ Technology Polymers (ITP) - *New Rules in the Polyolefins Structure/Rheology Relationship of Ethylene α -olefin Copolymers*, New Orleans, LA, May 1993.

The EXCEED™ m-E-polymer resin product now available from Exxon Chemical Company is a metallocene catalyst produced ethylene based copolymer. The processing of an EXCEED™ resin may be performed in a manner which is similar to that of conventional LLDPE with minimal equipment conversion required. A thermoplastic film made from an EXCEED™ resin has

demonstrated a 50 percent increase in puncture resistance and a 40 percent increase in tensile strength, as compared to a conventional polyethylene film.

One grade of EXCEED™ is a copolymer of ethylene and hexene-1 and is a linear polymer and a unique type of linear low density polyethylene. This metallocene produced m-E-polymer has a narrow molecular weight distribution (M_w/M_n), typically less than 3.0 while having useful weight average molecular weights (M_w) of greater than 10,000 and less than 500,000, and a narrow range of short chain branching (SCB) of about 12 and less than 30 SCB/1000 carbon atoms. The EXCEED™ class of polyethylenes (wherein the comonomer is a C_4 - C_8 alpha-olefin) have a substantial absence of low molecular weight and high comonomer content molecules, a substantial absence of high molecular weight and low comonomer content molecules, as indicated by CDBI ≥ 50 %; a narrow molecular weight distribution, and slightly lower melt strength than traditional linear ethylene polymers, and a slightly flatter shear rate viscosity curve.

Making A Film Layer

Blown films produced with an annular die and air cooling and cast films using a slot die and a chill-roll for cooling are both acceptable techniques for making a film layer of the m-E-polymer resin according to the present invention. Any technique may be used, provided the resulting film meets the specifications stated herein.

Additionally, various additives including pigments, plasticizers (?), tackifiers, anti-static agents, anti-fogging agents, antioxidants or other additives are also contemplated and may be included in the resins and/or films made therefrom.

Multilayered structures may be preferred in some applications. Such structures include, but are not limited to, coextruded films, and laminated films. Laminated films can include not only one or more film layers based on m-E-polymers of the present invention, but other film layers as well, including but not limited to, polyester, polyamide, polypropylene, other polyethylenes, Saran®, ethylene vinyl alcohol, and the like. Methods of lamination include extrusion lamination, adhesive lamination, heat lamination, and the like. Other materials may be laminated to final films structures of this invention, including films based on embodiments of the present invention, for instance paper, aluminum foil, paperboard, woven and non-woven materials.

Also contemplated are films where one or more layers are at least partially cross-linked by radiation. Such radiation and the techniques to achieve it are well known to those of ordinary skill in the art. These techniques include both gamma (cobalt 57) and x-ray radiation, electron beam and ultraviolet.

The film of the present invention can be any suitable thickness, depending upon the end use for the film. Typical thicknesses may range from about 3 microns to about 0.030 inches (0.25 mm) for a thin film to about 1 to 2 mm if a thick film is desired. The film can be obtained in a rollstock format for automatic form, fill and seal equipment or as preformed bags or pouches.

Making Oriented Film

The metallocene produced polyethylene films of this invention can be heat-shrinkable, that is an oriented m-E-polymer film can return to its original unstretched size when heated to its softening point. The terms "orientation" and "oriented" describe a manufacture of metallocene m-E-polymer heat shrinkable films. The m-E-polymer resin is heated to its flow or melting point and extruded through a die into either tubular (blown bubble) or sheet (cast) form and then cooled from its extrusion temperature. After cooling, the relatively thick extrudate is, as necessary, reheated to a temperature range suitable to orient or align the crystallites and/or molecules of the base m-E-polymer resin. An orientation temperature range for a given resin must be determined. The orientation temperature range is a range of temperatures in which the intermolecular configuration of the resin is revised by physical alignment of the crystallites and/or molecules of the resin to improve certain mechanical properties of the film, such as shrink tension as, for example, measured in accordance with ASTM D-2838-81.

While the m-E-polymer extrudate film layer is within the orientation temperature range, it is stretched, which changes intermolecular configuration, and then cooled while in the stretched or extended position. Cooling of the film stock while in the stretched position locks the crystallites and/or molecules of the material into a desirable configuration, providing an oriented film. Upon subsequent reheating to its softening point, as may occur during a packaging operation, forces within the film cause it to shrink essentially back to its original unstretched position. In this manner an oriented film is heat shrinkable, providing a shrink wrap film.

When the stretching force is applied in one direction, uniaxial or monoaxial orientation results. When the stretching force is applied in two directions, biaxial orientation (BO) results. In a continuous operation producing a rolled sheet of film, uniaxial orientation is typically provided by running a downstream roller at higher revolutions per minute than an immediately upstream roller, thereby stretching the film. This orients the film layer along its length in the machine direction (MD). Biaxial orientation is provided by also stretching the film layer along an axis at an angle to the uniaxial axis. Typically, biaxial orientation is provided by stretching in the machine direction and in a transverse direction (TD) at a right angle to the machine direction which is along

the width of the film layer. Transverse stretching can be provided by a machine called a TM Long or by a machine called a tenter frame stretcher.

A monoaxially oriented film typically refers to films oriented primarily in the longitudinal direction. However, some incidental orientation can be present in the transverse direction. The term can also refer to films oriented principally in the transverse direction, such as can be provided in a blown tubular film, with or without some incidental orientation in the longitudinal direction. A biaxially oriented film (BOF) for purposes of this application means a film the film layer of which, after its initial formation, is then intentionally and specifically oriented in the longitudinal direction (MD) and transverse direction (TD) by a degree that is beyond that which may be imparted a mere blown bubble process of forming the initial film layer itself, with the longitudinal direction being in the direction of the machine and transverse direction is the direction transverse to the machine. The biaxial stretching of the m-E-polymer film of the present invention can be carried out simultaneously or successively, with successive biaxial stretching being preferred, in which stretching is first carried out longitudinally then transversely. The preferred percentage of shrinkability of a film of this invention in the machine direction is 76%. This provides a film having good machinability and a wide sealing range.

Oriented m-E-polymer films may be produced by either post extruder manipulation of a blown film through heating and orientation (often called "double bubble" or "trapped bubble"), or by longitudinal stretching of an extruded sheet followed by tentering techniques. Orienting the film by a tentering technique is preferred since this generally produced a biaxially oriented film of superior mechanical/physical properties compared to orientation by a double bubble technique. Films after orientation are generally in the range of from about 0.2 to about 10 mils (5.08 to 254 μm) thick (gauge), preferably from 0.5 to 5 mils, and most preferably from 0.6 to 3 mils. Films layers formed by cast or blown bubble techniques to be produced into oriented structures will generally necessarily be thicker prior to orientation and will range from about 4 to about 25 mils. Choice of the thickness (gauge) prior to orientation will depend on orientation equipment, degree of intended orientation, and the properties intended of the film and/or resin. All such parameters are well within the skill and knowledge of those of ordinary skill in the art to determine, as a matter of routine setup, of a film line.

For purposes of this document, biaxial orientation will include orientations such as 2x2, 3x5, 5x5, 6x6, 7x7, 5x8 and the like. These notations will indicate a combination of film stretching in both the machine direction (MD) and transverse direction (TD) where 2 or 3, for instance indicate

200 or 300 percent difference in dimension after orientation. The amount of orientation need not be equal in both directions.

Film Properties

Compared to films made from previously known ethylene homopolymers copolymers or blends thereof, oriented m-E-polymer films made according to the present invention will generally be clearer, stiffer, stronger and exhibit greater shrinkage when heated. These stiffer, clearer and stronger BO-m-E-polymer-films may be used to make packages for crisp snacks, fresh meat, fresh produce, consumer soft and hard goods and the like.

Films made from the polymers of certain versions of the present invention may be used to contain food articles such as meats and snacks for instance. Such m-E-polymer so be used to protect and display articles of apparel and other consumer goods such as computer software, books, compact discs and a wide variety of magnetic storage media.

Various embodiments of the BO m-E-polymer films of the present invention have the following properties and ranges:

Haze	0 to 5, preferably 0 to 3, more preferably 0 to 2 %;
Gloss	greater than 70, preferably greater than 80, more preferably greater than 85;
Film densities	from 0.917 to 0.960 g/cm ³ ;
Dart Drop Impact	above about 400 g/mil at a resin desntiy of 0.917g/cm ³ ;
Peak Puncture Strength	greater than 40 lbs, preferably greater than 45 lbs/mil, more preferably above about 50 lbs/mil;
Puncture Break Energy	greater than about 25, preferably greater than 30 in-lb/mil;
Oxygen transmission (OTR)	less than 600, preferably less than about 550, and more preferably less than about 500 cc-mil/100in ² -atm/24 hrs; and
Water Vapor Transmission Rate (WVTR)	less than about 1, preferably less than about 0.9, and more preferably equal to or less than about 0.8 g-mil/100 in ² -24 hrs.

With ethylene polymers of certain embodiments of this invention it will be possible to design final film properties broadly by controlling polymer properties such as density. For instance, in lower density ranges, e.g. 0.917 - 0.925, preferably 0.917 - 0.920 g/cm³, biaxially oriented (BO) m-E-polymer films will be relatively soft, but strong and with excellent clarity. These lower density

BO m-E-polymer films will compete favorably with plasticized PVC films in applications such as meat wrap. On the other end of the spectrum, at higher densities, e.g. 0.920 - 0.960, preferably 0.925 to 0.950 g/cm³, BO m-E-polymer films fabricated from these ethylene polymers will have a high modulus and be very stiff and have excellent clarity. These BO higher density m-E-polymer films will compete favorably with biaxially oriented polypropylene in either single or multiple layers in applications such as snack and cereal packaging.

For a given m-E-polymer density, the biaxially oriented films of the present invention exhibit many improved physical properties as compared to substantially unoriented films such as standard blown or cast films. In addition biaxially oriented m-E-polymer films of this invention have better optical properties, exhibiting excellent clarity. Tensile at yield for these biaxially oriented m-E-polymer films can be expected to be 120-300% (MD) or 150-600% (TD) minimum greater than tensile at yield for a substantially unoriented film.

Oriented films based on the ethylene polymers of the present invention may find applicability in retail fresh meat packaging. In such packaging the meat is often placed in a tray, frequently made of foamed polystyrene and then typically over-wrapped with a plasticized PVC film. Attempts in the past to utilize polyolefins, more specifically ethylene polymers, have centered around improving the ethylene polymer's recovery to equal or exceed that of PVC. However, oriented m-E-polymer films according to the present invention do not depend upon recovery. Instead, these oriented films are relatively unyielding and thus are unlikely to indent under normal handling. These films are resistant enough to stress to successfully resist indentation, which is exemplified by their high tensile at yield. Although these films are relatively unyielding, the films are still soft enough to allow easy wrapping and thus will compete favorably against plasticized PVC film in these applications.

Shrink Wrap Films

Film of the present invention offers improved performance in the shrink-wrap market. The film includes at least one layer comprised of a polymer of ethylene polymerized in with a metallocene catalyst in the presence of a C₃ to C₈ alpha-olefin comonomer. Preferably, the layer is selected from an ethylene alpha-olefin copolymer having a density of and above 0.917 g/cm³ wherein the comonomer is a C₄-C₈ alpha-olefin. The final film may have multiple layers, and the thickness of the layers may be reduced without changing the product quality.

Each layer of the shrink wrap film is preferably comprised of a resin manufactured using a single-site catalyst, a metallocene. The shrink wrap film is preferably comprised of a metallocene produced linear low density polyethylene (m-LLDPE) resin of density from about 0.917 to about 0.940 g/cm³ which is cast or blown to a film layer that is then oriented in the MD and TD to produce

products such as stretch film, heavy-duty shipping sacks, flexible processed-meat packaging, poultry bags and the like. A preferred use of the BO-m-LLDPE film is shrink wrapping products such as compact discs. This improved film exhibits an increase in puncture resistance and an increased tensile strength over the existing films used for shrink wrapping. Additional layers can include, as desired, a barrier or oxygen layer for shrink wrapping food products and pallets of food. If the film structure is more than one layer, the layers can be joined by any suitable means. Co-extrusion is preferred.

For purposes of this application a m-LLDPE is an ethylene-alpha-olefin random copolymer having densities preferably from about 0.917 to 0.940 g/cm³. The alpha-olefin comonomer used in m-LLDPE is usually butene-1, hexene-1 or octene-1; however, other comonomers can be used, such as 5-methyl-1-pentene, or any other C₃-C₈ alpha olefin. Branches of the preferred m-LLDPE are short chain branches, 6 carbons and less, due to the comonomer, and the m-LLDPEs do not have many long branches off the main chain. The branching of this resin controls density and crystallinity. The preferred density of the metallocene LLDPE used in the film structure of the present invention is 0.917 to 0.924 g/cm³. The shrink wrap films of the present invention comprised of such m-LLDPE exhibit improved haze and gloss.

The metallocene LLDPE biaxially oriented film of the present invention meets the requirements of the shrink wrap industry by having excellent stretch and resistance to deformation and being resistant to abrasion. Thus, the film of the present invention has good machinability, adequate slip properties and is resistant to burn through.

For the shrink-wrap market, biaxially oriented films made according to the present invention offer superior properties. The biaxially oriented films shrink more, and this property, combined with other desirable properties, makes these BO-m-LLDPE films desirable for the shrink-wrap market.

Higher Density BO-m-E-Polymer Films

Films of the present invention may also comprises a biaxially-oriented high density polyethylene (HDPE) based on a metallocene or single-site catalyst (m-HDPE). The preferred density of the metallocene HDPE used in this film structure of the present invention is 0.925 to 0.960 g/cm³. This film exhibits greater impact strength, improved puncture resistance, and improved optics in haze and gloss as compared to a traditional ZN-HDPE.

The biaxially oriented film of the present invention has at least one layer comprised of m-HDPE that can be used as a replacement for certain applications involving polypropylene or nylon. A m-HDPE film can be used as a barrier layer in multilayer films for packaging or for skin packaging films. The m-HDPE film of the present invention has a high molecular weight and is

extrusion blown, and as biaxially oriented it can be used to produce clear shopping bags for use in a retail application. This BO-m-HDPE film can also replace polyethylene-nylon structures for uses as containers for food, medicine and the like.

A m-HDPE film can preferably undergo a blown film extrusion process with at least one additional film layer. The resulting film is a thin gauge, single or multilayer m-HDPE film with good heat seal performance, excellent strength and uniform thickness or roll quality.

Industrial applicability

Films according to the present invention are especially useful for packaging individually wrapped items, for instance, musical compact discs, software computer packages, musical tapes, and pallets of bulk items. However, the invention is not necessarily limited by the product contained within a package made from the inventive film as the film can suitably be used whenever a "wrapping" is desired, such as for winterizing windows from the influx of cold air.

Furthermore, the inventive film and packages therefrom exhibit excellent clarity and seal strength. Thus, the inventive film and packages are suitable for the food service industry (e.g., hospitals, schools, restaurants, fast food, etc.) and the shrink wrapping industry (e.g., stretch film used in the retail music business, computer software business, toy business, and the construction business) where appearance and seal strength are especially important and long shelf-life may be required.

Numerous applications are contemplated for these biaxially oriented m-E-polymer films of the present invention. The high clarity, variable stiffness, and the engineerable oxygen (OTR) and water vapor transmission rates (WVTR) make these films highly advantageous in applications such as modified-atmosphere packaging for fresh fruits, vegetables, meats and the like. These biaxially oriented m-E polymer films conform to the contours of products very well as compared to, for instance, oriented polypropylene. Thus, these biaxially oriented m-E polymer films are desirable as label stock (pressure sensitive, adhesive and the like).

These biaxially oriented m-E polymer films can have a relatively high one-percent secant modulus, which means that these films can be relatively stiff. Further, these films have a relatively low water vapor transfer rate (WVTR), which is good for keeping dry foods dry and moist foods moist. The stiffness of these BO-m-E polymer films conveys a sense of crispness, making these films desirable for packaging dry snacks such as cookies, crackers, potato chips, corn chips, peanuts, pretzels and the like, while the low WVTR keeps the snacks dry and crisp. Similarly, these films are well suited for applications including cereal packaging as an inside liner/container, particularly

since these films can be heat sealed. For such applications either single or multilayer films and/or bags can be used.

The high percentage shrink and the low oxygen transfer rate (OTR) makes the biaxially oriented m-E-polymer films particularly well suited for shrink-wrap packaging of fresh, cooked, and processed meats, poultry, fish, and the like, as well as other moist foods subject to spoilage.

These films can be metallized for packaging of foods and for decorative applications, and/or they can be made opaque for packaging, for instance, candy bars. On the other hand there are numerous nonpackaging applications for which these films are suitable such as for document or photo protective covers.

The package formed from the film structure of the present invention can also contain resealing means positioned away from a peripheral heat seal. For instance, a slot means can be provided on one interior face and tab means on an opposing interior face of the package such that after the heat seal is cut away, a consumer can reseal the package by pressing the tab into mating engagement with the slot. Such resealing means or slot and tab means are existing in the art.

Printing can be applied directly to the film if desired and ink can be imparted to the film by a flexographic or rotogravure apparatus. For food packaging the ink employed must be suitable for the application. The printing can be placed upon an outer or inner exposed surface or upon an inner surface of a multilayer film.

To make a package easier to open, a tear line can be provided. The film can be laser scored to form a single line or parallel lines of weakness in at least one layer of film of the present invention by partially vaporizing the film with a beam of radiant energy. The score lines form a tear path in a multilayer film. When the film is formed in a package, the score line may extend across the entire surface of the film.

EXAMPLES

A series of films were made and subsequently oriented by a tenter frame process. The properties of both oriented and non-oriented films (UO) were compared. To further demonstrate the differences, comparisons to commercial clear films were also included.

Definitions and Test Protocols

For the purposes of this application, parameters and tests referenced herein are defined as provided in Table 1. A procedure for measuring shrinkage is provided below.

Table 1.

<u>Property</u>	<u>Units</u>	<u>Definition or Test</u>
Density (d)	g/cm ³	ASTM D-792
CDBI	%	described within
Melt Index (MI)	dg/min	ASTM-1238(E)
Molecular weight distribution (MWD)	none	GPC
I ₂₁ /I ₂ (MIR)	none	ASTM D-1238
Haze	%	ASTM D-1003
Gloss	%	ASTM D-2457
Dart Drop Impact F ₅₀	g/mil	ASTM D-1709
Puncture (peak and break energy)	lb and in-lb/mil	Exxon Method
Oxygen Transmission Rate (OTR)	cm ³ -mil/100 in ² atm. /24 hrs @ 25°C	Exxon Method
Water Vapor Transmission Rate (WVTR)	g-mil/100 in ² /day (@ 38°C)	(ASTM E96)
Tensile at Yield	K psi	ASTM D-882
Elongation at Yield	%	ASTM D-882
Ultimate Tensile (at Break)	K psi	ASTM D-882
Elongation at Break	%	ASTM D-882
Secant Modulus (1%)	K psi	ASTM D-882
Elmendorf Tear	g/mil	ASTM D-1922
Shrinkage	%	Described below

To measure shrinkage, condition a sample at $23 \pm 2^\circ \text{C}$ and $50 \pm 5\%$ relative humidity for at least 16 hours prior to testing and 40 hours following fabrication. From a clean, wrinkle-free portion of the film sample, cut three to five circular specimens using a 100 mm circular die. The specimens should be representative of the entire film width. Draw a line on each specimen indicating machine direction (MD).

Rub a small amount of talc on a heat resistant tile and preheat the tile for uniform test results. Place a film specimen on the preheated tile using tweezers. Center a heat gun one to two inches over the sample and turn on the heat gun for about 45 seconds. Shrinkage will begin immediately, and ultimate shrinkage occurs after about 10-45 seconds depending on film thickness. Cool the sample with air. Repeat this procedure for each specimen. Measure each specimen along the line indicating the machine direction and subtract the length in mm from 100 mm to yield a percent shrinkage in

the machine direction. To determine a percent shrinkage in a transverse direction, repeat the measurements along a transverse axis.

Example 1

Exceed® 301 (now EXCEED® 357C32), an ethylene copolymer with hexene-1 manufactured with a metallocene catalyst by Exxon Chemical Co., Baytown, Texas, having a 0.917 g/cm³ density, a 3.4 melt index and having a peak melting point of 115°C (by DSC), was cast into a 15 mil film on a Killion extruder. Subsequently, the film was placed in a T.M. Long film stretch laboratory tenter frame orientation device and oriented to 5x5, indicating the amount of orientation or stretch in the machine direction (MD) and transverse direction (TD), respectively. The stretcher was manufactured by T.M. Long of 405 Bridge Street, Summerville, NJ 07986. Orientation temperatures used were 235, 245 and 250°F. These BO-m-E-polymer films, by comparison to an unoriented film cast (cast-UO) of the same m-E-polymer (EXCEED 301) to a gauge comparable to that obtained in the BO-m-E-polymer films, had nearly comparable haze and gloss properties as the cast film but otherwise the physical strength properties (tensile and secant modulus) of the BO-m-E-polymer films were dramatically improved. The tensile at yield (TD) improved by 200 to 300%, and the secant modulus improved by 150 to 200% (MD or TD). Tensile at yield, elongation at yield, and ultimate tensile all were improved by the orientation, while Elmendorf tear, as may have been expected, worsened with orientation. As compared to blown films of EXCEED® 301 this biaxial orientation improved clarity, tensile at yield, and secant modulus.

Example 2

A film sample from EDC 103 (now EXCEED® 350D60), an ethylene-hexene copolymer of density 0.917 g/cm³, 1.0 melt index, 17.2 melt index ratio, CDBI about 58, MWD about 2.3, and peak melting point 118°C (by DSC) manufactured by Exxon Chemical Co., Baytown, Texas, was made to a gauge of 1.62 mil and a 5 x 8 biaxial orientation. Two films of the EXCEED 350 D60 resin were also made by a blown bubble process, one to a greater gauge (3 mil) and the other to a lower gauge (0.8) than that of the oriented film and these blown films (blown-UO) were not thereafter oriented. Fig. 1 is a radar plot that compares the final film properties measured for the BO Em-E-polymerfilm and the unoriented blown m-E-polymer film of 0.8 mil gauge.

Example 3

A biaxially oriented polypropylene (BOPP) film commercially available as Bicolor®B from Mobil Chemical Co., Beaumont, Texas, and is believed to be based on a homopolymer polypropylene is compared in its properties with respect to a 5 x 8 biaxially oriented film of EDC 103 (or EXCEED 350 D60) at 1.62 mil gauge vs. Bicolor B® at 1.25 mil in Figure 2. Compared to

the oriented film prepared from EDC 103, an ethylene-hexene copolymer of 3 mole % hexene, $d = 0.917 \text{ g/cm}^3$, $MI = 1$ prepared from a metallocene catalyst, the BO EDC 103 film, by comparison to the BOPP film, exhibited reduced haze and 1 % secant modulus; comparable tensile strength and WVTR, greater Elmendorf tear strength and OTR.

Example 4

Two film samples, Exceed® 377X600, an ethylene copolymer with hexene-1, having a 0.922 g/cm^3 density and Exceed® 399X60, an ethylene copolymer with hexene-1, having a 0.926 g/cm^3 density, were biaxially oriented to a 6 x 6 degree using a T.M. Long stretcher. For the Exceed® 377X 60 sample, haze improved from 17.7 for an unoriented blown film to 1.1 % for a biaxially oriented film, while for the Exceed®, 399 x 60 sample, haze improved from 13.8 to 2.9 % compared to its blown film analogue. The biaxial orientation caused both orient films to become much stiffer, as indicated by a higher one-percent secant modulus. For both film samples the tensile strength at yield and the ultimate tensile strength increased significantly with orientation.

Example 5

Exceed®301 (now EXCEED 357 C 32) , an ethylene-hexene copolymer of 3 mole % hexene, density 0.917 g/cm^3 , melt index of 3.4 was processed by the procedure of Example 1 into a 5 x 5 biaxially oriented film and its mechanical/physical/chemical properties were determined, including its WVTR. A film of comparable WVTR comprising a HDPE ($d = 0.96 \text{ g/cm}^3$) prepared by a blown bubble procedure (and commercially available from Exxon and employed for various services) -- such as is the case for preparing cereal box liner films of an HDPE -- and the properties of the blown HDPE film were determined. Figure 3 presents a comparison of the properties of the respective films wherein between the two film samples the highest value of a film property is assigned as 100% and the value of that property in the other film is plotted as a percentage of that highest film property value. Accordingly, as shown by Figure 3, the WVTR value of each film is 100%. The biaxially oriented Exceed® 301 film had the greatest dart impact and Elmendorf tear resistance (the HDPE film being of less than 15% of these values) and the least haze (plotted as $1/\text{HAZE}$). The HDPE film had the greatest secant modulus, with the biaxially oriented Exceed® 301 film having about 35 % of the secant modulus of the HDPE film. The comparison establishes that a biaxially oriented m-E-polymer film of this invention would be a ready and desirable replacement film for HDPE films now made for service as cereal box liner films.

Example 6

EXCEED polymers of three differing densities; namely EXCEED 350 D60 of density 0.917 g/cm^3 , EXCEED 377 X 60 of density 0.922 g/cm^3 and EXCEED 399 X 60 of density 0.926 g/cm^3 ;

were produced as biaxially oriented films wherein the EXCEED 350 D60 was 5 x 8 oriented and the other films were 6 x 6 oriented films. Radar plot Fig. 4 illustrates the relative differences in the properties for these films.

Table 2 hereafter identifies the resin and film properties respecting all cast, blown and biaxially oriented films that were prepared and reported by these Examples 1-6.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, films, especially oriented films, have been exemplified in the present application. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred version contained herein.

CLAIMS

We claim:

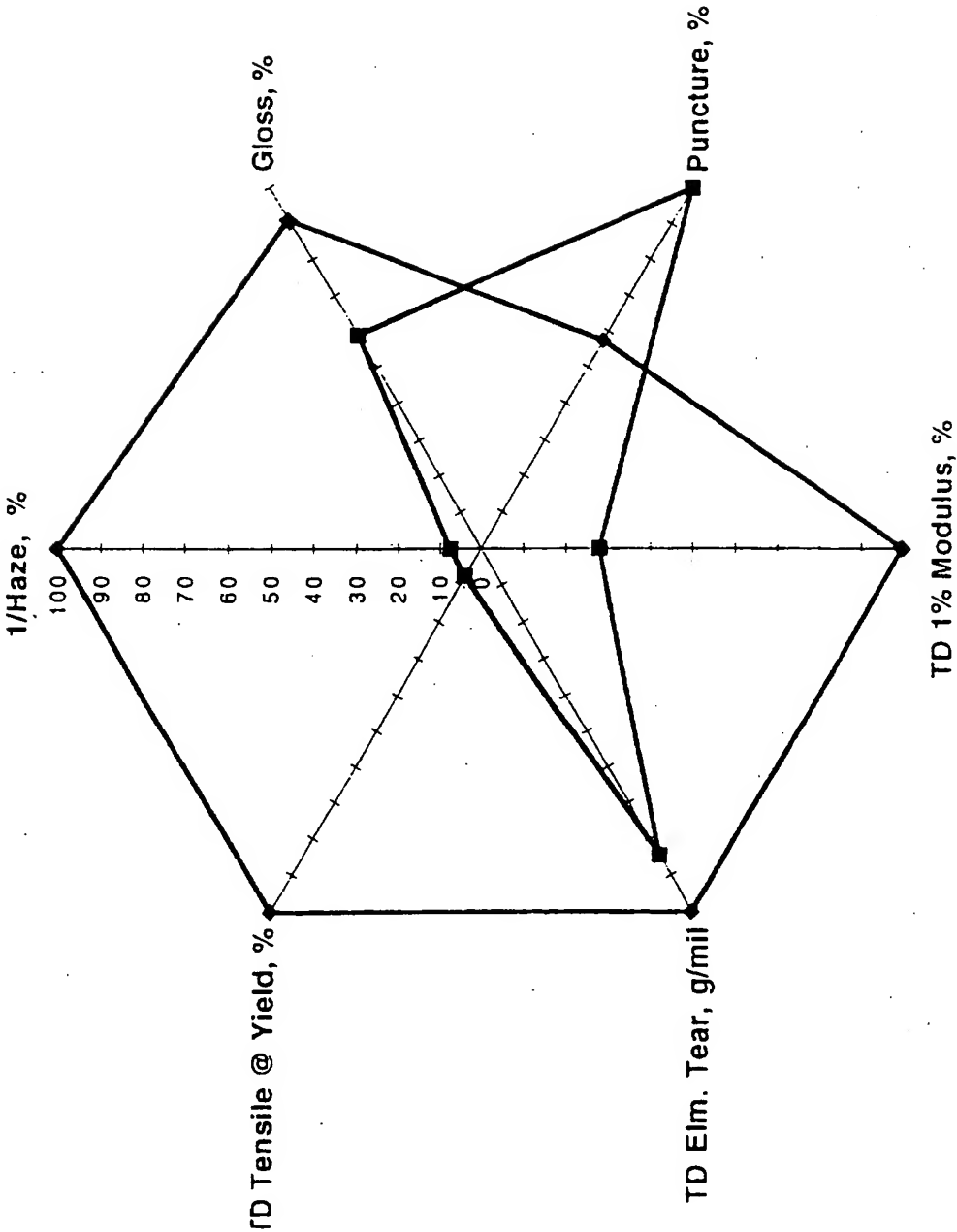
1. A film, comprising; a biaxially oriented film layer composed of a thermoplastic ethylene polymer having an ethylene content of greater than 90 wt%, a CDBI greater than 50%, a content of 0 to 6.0 mole % of a C_3 - C_{20} alpha-olefin comonomer and a density of 0.915 g/cc or greater.
2. A film, comprising; a biaxially oriented film layer which comprises a thermoplastic consisting of an ethylene polymer having an ethylene content of greater than 90 wt %, a CDBI greater than 50%, a content of 0 to 6.0 mole % of a C_3 - C_{20} alpha-olefin comonomer and a density of 0.915 g/cc or greater.
3. A film, comprising; a biaxially oriented film layer composed of a metallocene catalyzed ethylene polymer having an ethylene content of 90 wt % or greater, a density of from about 0.917 to about 0.95 g/cm³, a CDBI greater than about 50%, a content of 0.01 to 5.0 mole % of a C_4 - C_8 comonomer.
4. The biaxially oriented film of claim 1, wherein said ethylene polymer has a M_w/M_n less than about 3, and a M_z/M_w less than about 2.
5. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized using a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a secant modulus of at least 25,000 psi.
6. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a haze less than 5 %.
7. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a tensile strength at yield greater than 1,800 psi.

8. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer shrinking at least 40 % when heated to a softening point.

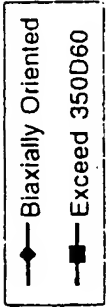
9. A film, comprising; a biaxially oriented film layer formed of a thermoplastic ethylene polymer resin having an ethylene content of greater than 90 wt %, a CDBI greater than 50 %, a content of 0 to 6.0 mole % of a C₃-C₂₀ alpha-olefin comonomer and a resin density of at least 0.915 g/cm³, wherein density of the biaxially oriented film layer is greater than the density of the resin from which said film layer was formed.

FIGURE 1

Biaxially Oriented v Blown Exceed
0.917/1 MI; 350D60



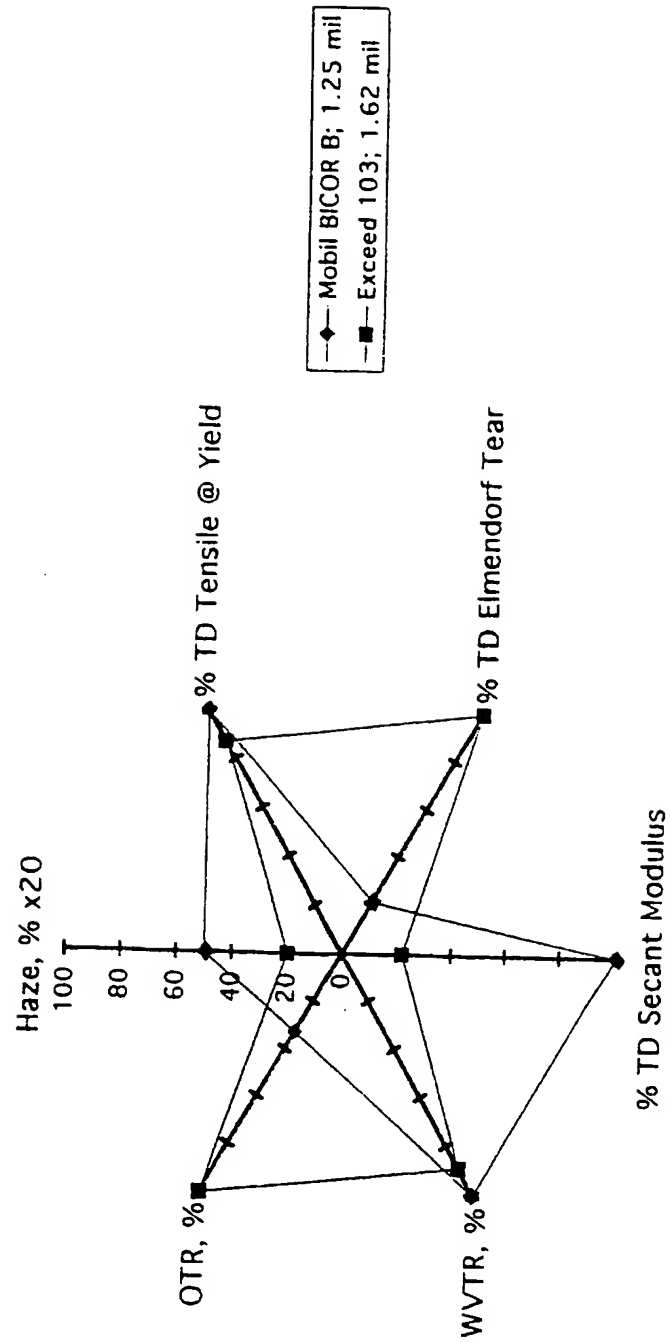
1/4



2/4

FIGURE 2

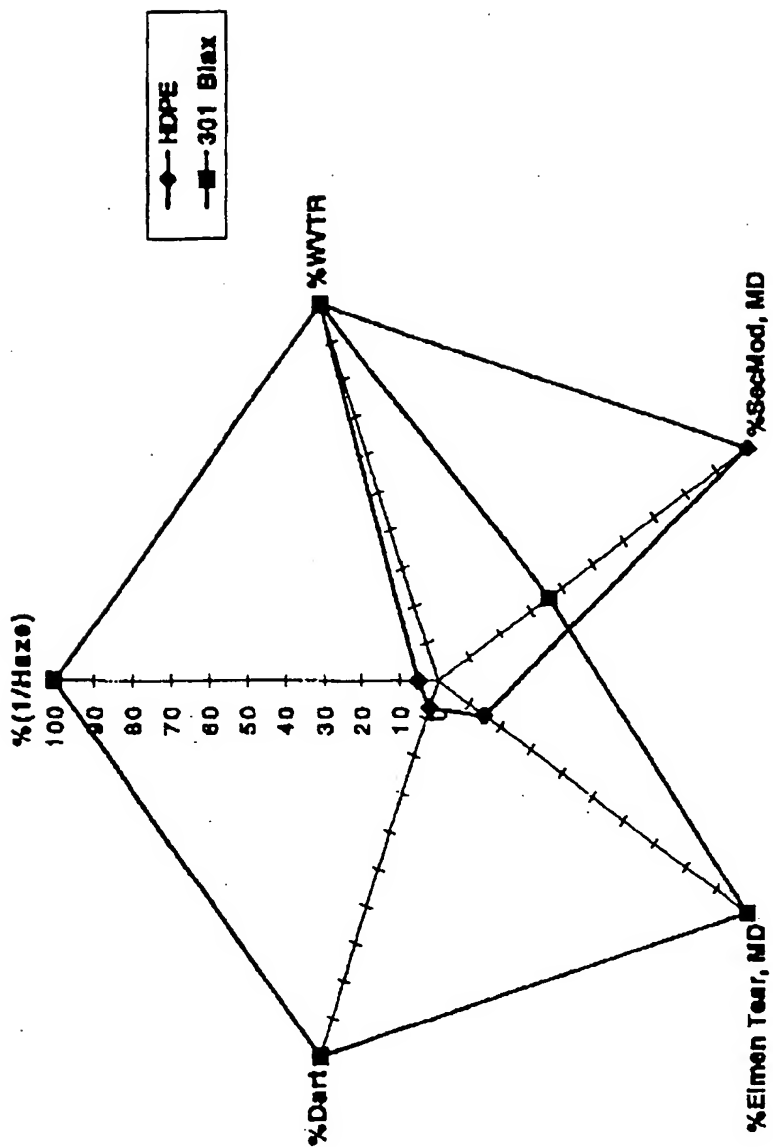
Properties Comparison: Biaxially Oriented Exceed v Polypropylene



3/4

FIGURE 3

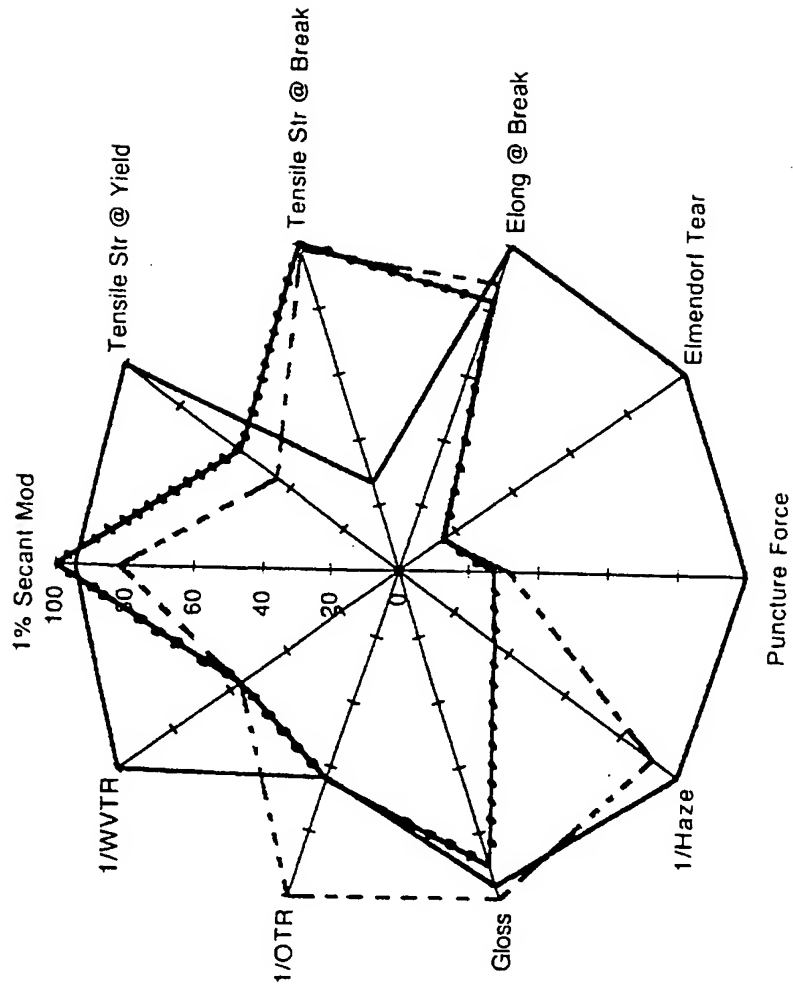
Properties Comparison: Cereal Liner Application



4/4

FIGURE 4

Properties Comparison for Biaxially Oriented Exceeds



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20180

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

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U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,397,640 A (GEORGELOS et al.) 14 March 1995, see entire document.	1-9
X, P	US 5,562,958 A (WALTON et al.) 08 October 1996, see entire document.	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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A. CLASSIFICATION OF SUBJECT MATTER:
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A. CLASSIFICATION OF SUBJECT MATTER:
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428/349, 516

B. FIELDS SEARCHED
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Classification System: U.S.

428/349, 516

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, JPOABS, EPOABS
search terms: polyethylene, oriented, metallocene



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<p>(21) International Application Number: PCT/US96/20180 (22) International Filing Date: 18 December 1996 (18.12.96) (30) Priority Data: 60/008,777 18 December 1995 (18.12.95) US 08/755,105 22 November 1996 (22.11.96) US (71) Applicants: EXXON CHEMICAL PATENTS INC. [US/US]; 1209 Orange Street, Wilmington, DE 19801 (US). EMPIRE FILMS DEVELOPMENT COMPANY [US/US]; 215 Miles Cutting Lane, Pittsford, NY 14534 (US). (72) Inventors: BRANT, Patrick; 103 Harborcrest, Seabrook, TX 77586 (US). BRACKEEN, James, H.; 14815 Tumbling Falls Court, Houston, TX 77062 (US). TRUDELL, Barry, Collin; 625 Esser Cres, Samia, Ontario N7S 5J2 (CA). RIRIE, James, I.; 50 Park Circle Drive, Fairport, NY 14450 (US). BATES, Monty, K.; 7571 Trotwood Lane, Victor, NY 14564 (US). FISCHER, David, C.; 215 Miles Cutting Lane, Pittsford, NY 14534 (US). (74) Agents: COX, Charles, M. et al.; Pravel, Hewitt, Kimball & Krieger, P.C., 10th floor, 1177 West Loop South, Houston, TX 77027-9095 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.</p>
<p>(54) Title: BIAXIALLY ORIENTED POLYETHYLENE FILMS (57) Abstract Articles and films are provided from ethylene-based polymers made using a metallocene catalyst system. Biaxial orientation dramatically improves clarity, stiffness, dart drop impact, puncture resistance, and shrink. Tensile strength at yield and ultimate tensile are also improved. Film stiffness, as measured by secant modulus, is increased by 300 % over an unoriented film of the same ethylene polymer. These articles and films are useful as shrink wrap, overwrap, and for dry packaging applications such as snacks and cereals as well as non-packaging applications such as photograph and document holders.</p>		

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BIAXIALLY ORIENTED POLYETHYLENE FILMS

This invention relates to a biaxially oriented film of an ethylene based polymer. More specifically, this invention relates to a film layer made from thermoplastic ethylene based homopolymer or random copolymer produced by a metallocene catalyst system, wherein the film layer is stretched in two directions for biaxial orientation.

Polymeric films are widely used, both in industrial manufacturing processes and in the non-industrial sector for the wholesale and retail delivery of goods to the consumer market. By far the greatest quantity of polymeric film, in film and bag form, is designed for, use and consumed by the non-industrial sector.

Currently, films composed of ethylene based thermoplastic polymers dominate certain of these consumer market applications -- such as the market for household disposables, trash bags and liners; overwrap films and bags for laundry and dry cleaning goods; and shipping and carryout bags for retail merchandising of non-perishable goods. In other aspects of the consumer goods delivery market, ethylene based polymer films only weakly compete, if at all, with other more expensive polymer films such as plasticized polyvinylchloride films and/or polypropylene films -- such as in the heat-shrink wrap film market for the taut-contour fit wrapping of various items, particularly perishables such as cuts of meat, poultry, and fish. Yet for other applications, such as for packaging of produce, package constructions for cereals, dry foods, and snack foods ethylene based polymer films compete somewhat in certain circumstances of these applications. At the wholesale level wherein films are used to unitize pallets and cases of goods to facilitate their shipment to a retail market current ethylene based polymer films are essentially uncompetitive with shrink-wrap and cling films of plasticized PVC or polypropylene.

Heat shrinkable films and packages thereof have gained substantial acceptance for wholesale and retail packaging of food products and goods. In the retail environment, packing films used to package food products and non-food products must be of high optical clarity (i.e., highly transparent and of low haze and, preferably high gloss) to provide an aesthetically pleasing product and must be sufficiently strong and resilient to provide the necessary protection from normal handling. Depending upon the nature of the packaged goods, the film must also possess proper barrier properties with respect to permeation by water vapor, oxygen, and/or carbon dioxide.

Successful heat shrink films and packages must satisfy a multiplicity of requirements imposed by both the packaging producer and the packaging user. Of primary importance is the capability of the film or package to physically survive intact through the process of being filled, evacuated, sealed and heat shrunk. The film package must also be strong enough to survive the

material handling involved along the distribution line to the ultimate user. In packaging foods such as meat, it is also highly desirable, even necessary, that the package film serve as a barrier to moderate and control infusion of gaseous materials (oxygen and carbon dioxide) from the surrounding environment. Of particular importance for packaging of meat products is that a film provide an effective barrier to the infusion of oxygen, since oxygen is well known to cause spoilage of meat. For bundling or unitizing non-perishable goods wherein oxygen permeation may be of less concern, the shrink wrap film must often serve a barrier function against water vapor permeation and should desirably possess a self-cling property.

Polyvinyl chloride (PVC) is now widely used for production of films used in overwrapping applications in the packaging field. PVC films are commonly used as an overwrap for trayed cuts of meat and other food products in a retail environment such as a supermarket. PVC is desirable for production of films for this service because it has excellent optics or clarity, good elasticity and strength properties at use temperatures, and satisfactory elastic memory ability and elongation. However, PVC resins have several disadvantages. PVC film has a poor resistance to physical abuse, and thus, a PVC-based film package sometimes becomes leaky during shipment. PVC film tends to tear along the edges of a sealed overwrap tray, for instance, if rubbed during transit by another tray or an enclosing carton. Furthermore, unless the PVC resin is plasticized films thereof are generally not "heat shrinkable," which means that after stretching the film while heated followed by cooling, under a later reheating an unplasticized PVC film tends not to return to its original unstretched dimension. If plasticized to enable the production of a heat shrinkable film, then significant concern has to be given to the nature of the plasticizer used, its quantity and compatibility with the PVC resin and migration of such plasticizer from a film thereof and its suitability for contact with foodstuffs.

The packaging industry, particularly for perishable food products and individually wrapped non-food items, desires a film having the advantages of PVC, but without the disadvantages described above. For such applications the film should be of high clarity, tear resistant, puncture resistant, and the film should exhibit resistance to deformation or good recovery from deformation and satisfy food law requirements.

The use of films of vinylidene chloride-vinyl chloride copolymer, introduced under the trademark Saran, is presently popular due to the physical characteristics of a film produced from such resin. It is clear, has a high tensile strength, forms a good barrier against moisture and vapor transmission, is mildew resistant, has good conformability to the item being wrapped, may be formulated for high slip, and it possesses an inherent self-adherability or "cling."

Vinylidene chloride-vinyl chloride copolymer films are typically formed by extruding the resin in the form of a blown tube which is then super cooled. This process of forming the initial film layer may cause a certain degree of orientation to occur in the film layer but (due to the relaxation properties of this resin) such residual orientation as may remain in the film layer due to its bubble extrusion forming is not typical of the morphology that subsequent stretching of the film layer in a machine direction (MD) induces. Such vinylidene chloride-vinyl chloride copolymer blown films may be subsequently oriented by stretching in a longitudinal or machine direction as a second bubble while the so produced film layer is still warm and soft after which it is cooled.

Unfortunately, a vinylidene chloride-vinyl chloride copolymer oriented film does not respond well to later applications of heat. Heat causes instantaneous film shrinkage because orientation is lost, heat seals with such films are not smooth, resulting in a weak seal. Furthermore, hot melt coatings of this oriented film with another polymeric material to produce a film composite or multilayer film having more desirable characteristics is not possible. The oriented film loses its orientation upon contact with a hot melt. In lamination, the hot press rolls usually cause the oriented film to react similarly.

Characteristics such as heat sealability are not the only criteria by which one evaluates a film structure for suitability to shrink wrap products such as compact discs, pallets of individually wrapped items, or the like. Strength and clarity are very important characteristics in such packaging. To obtain these desirable shrink characteristics, conventional shrink bags are today constructed of ethylene vinyl-acetate copolymers. These copolymers often have a vinylidene chloride - vinyl chloride or ethylene vinyl alcohol copolymer layer serving as a water vapor barrier. However, films from these resins tend to be soft and cloudy, rendering the film unsuitable with respect to appearance and vulnerable to failure at conditions of operation due to the relatively high temperatures to which it is exposed in the orientation and shrinking process.

By reason of their lower cost, ethylene homopolymers and copolymer resins and blends thereof enjoy widespread use in the packaging industry for certain applications. Typically, polyethylene (PE) resins employed as such or as a blend component in packaging are high density (HDPE), linear low density (LLDPE), low density (LDPE), very low density (VLDPE) or ultra low density (ULDPE). LLDPE, VLDPE and ULDPE are ethylene copolymer wherein, typically, the comonomer is a C_3 - C_{20} alpha-olefin. The comonomer introduces branching into the polymer and affects its density. These polyethylenes have been and still are typically made with traditional Ziegler-type catalysts which contain different types of reaction sites resulting in a polyethylene resin containing a broad range of molecules. For instance, such polyethylene typically contains polymers

having a medium molecular weight with medium branching fraction, a low molecular weight and high branching fraction, and high molecular weight with low branching fraction. This results in inconsistent properties, and sometimes, poor clarity when such resins are converted into films as well as certain difficulties in production of the film itself.

Today, many oriented polymeric films are of multiple layer construction and comprised of at least one barrier or oxygen layer, such as ethylene polyvinyl alcohol (EVOH) or vinylidene chloride-vinyl chloride copolymer, and a of different polyethylenes or of polyethylene layer such as LLDPE, HDPE, LDPE, VLDPE, or blends of polyethylene with acetates, such as ethylene-vinyl-acetate (EVA). This is because EVAs having greater than about 85 wt % ethylene provide substantial structural strength to a film during the second bubble orientation process, and are especially beneficial for the orientation of tubular films. Such multiple layer films are formed by a number of ways, including coextrusion, lamination and coating techniques.

A heat shrinkable film should be susceptible to orientation without distortion or separation of the multiple layers which are typically present in films of this nature. The film layer must be strong enough, at the orientation temperature, to withstand the stretching in either of the machine direction (MD) or transverse direction (TD) without the creation of holes, tears, or non-uniform zones of stretching. In the case of blown tubular film, the film layer must be capable of supporting the stretching bubble during the orientation process. With multi-layer film constructions, each layer of the film should be susceptible to orientation without fracture, separation, or creation of holes in the layer. In packaging use, the final film product should respond to heat rapidly enough for commercial practicality, and yet must not exhibit such a level of shrink energy as would cause the multiple layer film to pull apart or de-laminate during shrinkage under its own internal forces.

Preferably, oriented films used for shrink packaging should be clear enough for a consumer to visually inspect the packaged item prior to purchasing. If the packaging is cloudy (hazy) or not sufficiently transparent or translucent, a wrapped food item will appear to be undesirable to the consumer. Thus, clarity is a product attribute widely sought in many types of polymer films for certain application.

In the past, thermoplastic ethylene based polymers have not been adopted by the industry for applications that require softness, but with good shape retention or recovery (snapback). Polyethylene films, particularly those of a LDPE or LLDPE, have traditionally been relatively soft or limp, having a low secant modulus, and softness is a desirable property in some applications, such as for wrapping a meat product. This would appear to make polyethylene resins desirable for production of films for such services, which due to its lower density and cost, would desirably

displace PVC films from these services. However, polyethylenes have been largely unsuccessful in replacing PVC in at least the meat wrap application, primarily because a polyethylene film retains or recovers its shape poorly after handling, leaving unacceptable fingerprints on the film. PVC films, on the other hand, snaps back or recovers its shape a few minutes after handling, providing a fresh appearance.

In yet other applications, such as in packaging snack foods, such as potato chips, a film should feel stiff to protect and/or convey the crisp and crunchy nature of the product. The softness of an ethylene based polymer film has rendered it undesirable for this service. Today the film widely employed for snack food packaging is biaxially oriented polypropylene (BOPP) film due to its high degree of stiffness, its good optical properties of low haze and high gloss, and good barrier properties to water vapor transmission.

For fresh-cut produce, today modified atmosphere packages are desired. A modified atmosphere package (MAP) is one wherein the film material of its construction has breathing characteristics within specifically intended ranges relative to the transmissibility of the film to oxygen, carbon dioxide and water vapor. In a modified atmosphere package the transmissibility of a film to these vapors must neither be too low nor too high but should instead correspond of the "respiration" of the produce product for these vapors. For example, a film for MAP applications should have an oxygen transmission rate (OTR) of about 300-1200 cc mil/100 in² atm/day, a carbon dioxide transmission rate (CO₂TR) of about 1,000 to 5,000 cc mil/100 in²atm/day and, to prevent dry rot of produce, a water vapor transmission rate (WVTR) of less than 2.5 g mil/100 in²day. Resins widely used today for MAP applications are Ziegler catalyst produced VLDPE films despite their limited OTR and poor haze properties and EVA films despite their poorer WVTR properties.

Because an ethylene based polymer is generally a lower cost product, it has long been seen as a desirable goal to use a thermoplastic polyethylene for various uses that have been heretofore dominated by higher cost polymers. However, ethylene-based polymers heretofore available have lacked various properties required for a particular film service or were otherwise objectionable. For some applications, such as snack food packaging, polyethylene was considered too soft and lacking in stiffness. As a shrink wrap film, it has heretofore been necessary to form such films from the heretofore available polyethylene resins by a blown bubble extrusion process and then orient it by a double bubble procedure. Formation of a biaxially oriented film of polyethylene by a slot-die casting tenter frame stretching process in which the degree of orientation may be more varied and precisely controlled has not been practical due to the tackiness and inadequate melt strength and

excessive melt elasticity of a film layer of an ethylene polymer at the conditions required for tenter frame stretching.

Cast and blown bubble films prepared from the same ethylene polymer resin and to the same gauge differ dramatically with respect to their haze and gloss properties. Cast films have significantly lower haze and significantly higher gloss than do blown bubble films of the same ethylene polymer resin. In either case, cast or blown bubble films, as the density of the ethylene polymer resin of which the film is formed increases the haze of the film increases while its gloss decreases; with the rate of increase/decrease of haze/gloss with increasing resin density being significantly greater for blown bubble than for cast films.

In some cases, wherein good film optics are requisites for use of a film, low haze/high gloss properties may be obtained in a cast film of a low density ($d < 0.940 \text{ g/cm}^3$) ethylene polymer (LDPE or LLDPE); but such LDPE or LLDPE films are attended with a lower set of physical strength properties (tensile, elongation, tear resistance) than could be attained with a high density ($d \geq 0.940 \text{ g/cm}^3$) ethylene polymer (HDPE). Even then, such good optics cannot be attained with such low density ethylene polymers in a blown bubble film. On the other hand, wherein the physical strength properties required of a film exceeds those that can be obtained with a low density ethylene polymer, a high density ethylene polymer can be employed for the cast or blown bubble extrusion of a film to attain the requisite film strength properties but at a sacrifice of the film optics, with this sacrifice being much greater for blown bubble films.

Today such ethylene based polymer films that have been proposed as biaxially oriented heat shrinkable films are those prepared from a blend of a low density ethylene polymer of density from about 0.91 to 0.93 g/cm^3 and a high density ethylene polymer of density from about 0.940 to 0.98 g/cm^3 , as described for example in GB 937,807 and GB 1,279,714, or a low density ethylene polymer and a very low density ethylene polymer of density from about 0.87 to 0.910 g/cm^3 , as described for example in EP 0299750 and U.S. Patent 4,801,652. Even then such ethylene based polymer blend films have not been widely adopted for certain services such as food packaging because of certain real or perceived deficiencies in their properties and/or difficulties in their production.

Film producers and converters recognize that there is a need for a polyethylene (ethylene homopolymer and/or ethylene copolymer) that can be fabricated to a film form of high clarity and high stiffness and/or high clarity and good snapback. Further, a film produced from any polyethylene should have good impact and puncture resistance, increased tensile at yield and other physical properties, and low levels of extractables so as to not impart unpleasant odors or tastes to

a food product. Proper shrink properties are also desired for certain applications such as packaging certain food products and goods, covering windows, and wrapping meat pallets.

A film should have as few layers as possible, but with a desirable combination of properties. There is a need for a one-, two- or three- layer film structure that may be produced from a thermoplastic ethylene based polymer resin that has good clarity, high strength, and which can be readily heat sealed with a strong seal resulting and printed upon with protection for the printing, which may be biaxially oriented to yield a heat shrinkable film.

It has now been found that ethylene based polymers produced from a catalyst having essentially only one type of catalytic site may be fabricated into oriented films having improved properties with respect to heat sealability, greater impact strength, puncture resistance, and optimal optic properties such as haze and gloss. It has further been found that an ethylene based thermoplastic polymer produced with a metallocene catalyst may be fabricated into a film which can meet the needs of the food packaging industry, the pallet shrink-wrap industry, and the market for individual shrink wrapped goods.

This invention comprises a film layer formed by cast or blown bubble extrusion of a single ethylene polymer resin which is then biaxially oriented by a tenter frame or double bubble procedure to yield a biaxially oriented film layer that has good optical properties of low haze and high gloss -- like that of a cast extrusion LDPE film -- while exhibiting high strength properties -- like that of a cast or blown bubble extrusion HDPE film.

It has been found that certain ethylene homopolymers and copolymers (ethylene based polymers) made utilizing metallocene catalysts, after being made into a film and subsequently oriented in at least two directions show a surprising ability to withstand such orientation, as well as displaying enhancements in important physical properties after such orientation, when compared to other previously known ethylene polymers in general, and linear low density polyethylenes (LLDPE) in particular, most especially those polyethylenes made using traditional Ziegler-Natta catalysts. In one embodiment of the present invention, the most striking improvements are evidenced in clarity (manifested in haze and gloss), dart drop impact resistance, puncture resistance, oxygen and water vapor transmission rates, tensile at yield, secant modulus, and the like.

In an embodiment of the present invention, extruded articles such as film, or other fabricated articles made from such film, are comprised of an ethylene homopolymer or a copolymer of ethylene and at least one C₃-C₂₀ alpha-olefin. The alpha-olefin of the copolymer is present in the range of from about 0.01 to about 6.0 mole percent of the copolymer, for C₄-C₂₀ alpha-olefins preferably no greater than 5.0 mole %. The ethylene based polymer will have a content of ethylene greater than

90 wt%, a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) of $M_w/M_n \leq 3$, a ratio of a Z - average molecular weight (M_z) to weight average molecular weight of $M_z/M_w \leq 2$, a composition breadth distribution index (CDBI) of 50% or preferably greater, such as 55 %, a density in the range of from about 0.915 to about 0.965 g/cm³, an I_{21}/I_2 melt index ratio (MIR) of less than about 22, a Dow Rheological Index (DRI) of < 0.3 , and a peak melting point (DSC) from about 103-135°C.

Biaxially oriented film made from such ethylene based polymers will exhibit certain film properties that are relatively sensitive to a change of polymer density, such as

- (a) Secant Modulus (MD/TD), which increases with increasing density;
- (b) Tensile Strength at Yield, which increases with increasing density;
- (c) Elongation at Break, which decreases with increasing density;
- (d) Oxygen Transmission Rate (OTR);
- (e) Water Vapor Transmission Rate (WVTR);

film properties that are relatively sensitive to resin density changes from about 0.915 to about 0.930 g/cm³ and thereafter relatively insensitive to density changes beyond 0.930 g/cm³, such as

- (f) Tensile strength at Break;
- (g) Elmendorf Tear;
- (h) Puncture Strength;
- (i) Dart Impact Strength, which is greatest at the 0.917 to 0.922 g/cm³ density range, and declines significantly by comparison as density increases beyond 0.922 g/cm³;

and film properties that are somewhat insensitive to a change in polymer density, such as

- (j) Haze;
- (k) Gloss;
- (l) Shrinkage.

Further, with an ethylene based polymer of an appropriately selected density, a film may be engineered to provide a target or desired property value relating to film strength, vapor barrier properties and the like by appropriately controlling the conditions and degree of orientation imparted to it in the MD and TD.

In certain embodiments of the invention a biaxially oriented film comprised of such ethylene based polymers will exhibit properties such as:

- a) haze in the range of from 0 to 5%;
- b) gloss above about 65%;

- c) dart drop impact above 400 g/mil at a resin density of 0.917 g/cm³ and no lower than 150 at a resin density of 0.940 g/cm³;
- d) oxygen transmission rate below about 600 cc-mil/100 in²-atm/24 hours @ 25°C;
- e) a tensile at yield of 2000 psi or greater (MD) or 5000 psi or greater (TD);
- f) a secant modulus (1%) above about 40,000 psi (MD), or above about 70,000 psi (TD) and;
- g) shrinkage of at least 10% in each of the oriented directions.

Those of ordinary skill in the art will understand that for a given polymer at a given temperature, the more highly oriented film will shrink more than a film of lower orientation (at same temperature and base polymer density). Shrinkage will occur at a temperature range of 70° to 90°C within 10 seconds, preferably the shrinkage occurs in a temperature range of 75 to 85° within 5 seconds.

Shrink films made from such ethylene homopolymers and ethylene-alpha-olefin copolymers and articles made from these films will be particularly useful in applications where maximizing optical properties, secant modulus, impact resistance, puncture resistance and the like are important.

Thus, one preferred embodiment of the present invention provides an ethylene based polymer film having an oxygen permeability no greater than about 500 and typically about 150-450 cc/100 in²/24hr. The film comprises a biaxially oriented (BO) film having increased optical clarity, puncture resistance and tensile strength, said film comprising at least one layer of an ethylene copolymer thermoplastic resin produced from a metallocene catalyst and having an ethylene content of greater than 90 wt%, a density range from 0.915 g/cm³ to about 0.930 g/cm³. The film layer is biaxially orientable to an extent of 5 x 8 or 7 x 7 (MD x TD). The biaxially oriented film (BOF) is heat shrinkable and more preferably exhibits a 76% shrink in the machine direction. In addition, the film is 100% recyclable.

Another preferred embodiment of the present invention also provides a biaxially oriented (BO) film comprising at least one layer of linear low density ethylene-alpha-olefin copolymer density of 0.915 to 0.940 g/cm³ polymerized with a metallocene catalyst, which may hereafter be referred to as a "m-LLDPE" resin. The m-LLDPE film has improved optical clarity and physical toughness for biaxial orientation, and optionally may comprise a second and third layer. In a preferred embodiment, the BO-m-LLDPE-film includes a first layer and a second layer that are co-extruded. The BO-m-LLDPE-film can also include a fourth layer adhesively laminated to the third layer.

The present invention also comprehends packages fabricated from the films of the invention wherein the second or third layer is heat sealed. The invention further includes a method for

packaging a product such as a compact disc or software package and shrink wrapping the product in a package made from the BO-m-LLPDE-film of the present invention. In addition, the invention comprehends a method for wrapping an item, preferably a window frame or door frame comprised of the film of the present invention.

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings.

A radar plot or diagram is a multiple axis (≥ 3) graphs wherein each radiating axis from the center point of its origin to its end point represents a range of values -- either actual or as a percentage of an assigned maximum value (relative) -- with each axis representing the value range of a different chemical/mechanical/physical property of the final film product or the film resin, as may be indicated on the plot. In this respect the differences and/or similarities between one film and another, or the relationship between a change in resin property to a change in a final film property (actual or relative) may readily be viewed and assessed.

Fig. 1 is a radar plot by which the final film properties of an m-E-polymer BO film of 1.62 mil thickness and 5 x 8 orientation of this invention is compared on a relative basis to a blown but unoriented m-E-polymer film prepared from the same resin, namely EXCEED 350 D60.

Fig. 2 is a radar plot by which the final film properties of an m-E-polymer (EXCEED 350 D60) BO film of 1.62 mil thickness and 5 x 8 orientation of this invention is compared on a relative basis to a commercially available film of biaxially oriented polypropylene (BICOR®B, from Mobil Chemical Co.).

Fig. 3 is a radar plot by which on a relative basis the final film properties of an m-E-polymer (EXCEED 301) BO film of 5 x 5 orientation of this invention is compared to a blown film of a high density polyethylene.

Fig. 4 is a radar plot by which on a relative basis the final film properties of three BO films of EXCEED resins of different densities (0.917; 0.922; 0.926-g/cm³) are compared; the 0.917 g/cm³ density resin BO film (350 D60) being of 5 x 8 BO and 1.62 mil gauge and the other films being of 6 x 6 BO and 0.6 mil gauge.

The present invention comprises the utilization of ethylene based polymers having certain minimum characteristics with respect to their ethylene content; molecular weight, both M_w and M_n ; their density; and the compositional uniformity of the ethylene based polymer resin: for the production of a film layer which upon biaxial orientation yields a film article having a set of physical/mechanical/chemical properties requisite to the service required of such film for various

particular applications which heretofore have not been particularly serviceable by an ethylene based polymer film.

The present invention concerns certain classes of biaxially oriented films fabricated from ethylene based polymers made utilizing a metallocene catalyst system, articles made from these films, and uses of the films and/or articles. For purposes of this application, such ethylene based polymers include ethylene homopolymers and ethylene copolymers in which ethylene is the predominate monomeric constituent by weight or mole %; specifically, ethylene comprises at least and preferably more than 90 wt % of the ethylene based polymer while the comonomer content thereof does not exceed 6.0 mole % of the ethylene based polymer and the CDBI of the polymer exceeds 50%. Preferably such ethylene based polymers comprise at least about 93 wt % ethylene monomeric units and the comonomer content thereof does not exceed 5.0 mole % and more preferably the comonomer content does not exceed about 3.3 mole % of the ethylene based polymer. Such ethylene based polymers may hereafter be referred to generally as an "m-polyethylene" or as an "m-E-polymer."

The term "oriented" means that the m-E-polymer film has been stretched while in a softened state while at a temperature below that at which the film layer was initially extruded by a cast or blown bubble technique, and "biaxially" means that the cast or blown bubble m-E-polymer film has been stretched in both of a machine direction (MD) and a direction transverse to the machine direction (TD), as described further below. The degree of biaxial orientation is denoted as the percentage as compared to the original dimensions of the extrusion formed film layer that the film layer is stretched; i.e., such as 100;200...600 % of its original dimension of length (MD) or width (TD). For example 1x1 orientation means that the initial film layer has been stretched to twice its original dimension in each of the machine direction (MD-length) and transverse direction (TD-width); 6x6 would denote a stretching to six times the original length and width dimensions of the initially formed film layer. Films produced of the particular ethylene based polymer in their biaxially oriented form have unique characteristics, which may be manipulated by the degree of or type of orientation, which make them well suited for use in certain service applications.

The term ethylene copolymer as used herein shall mean copolymers of ethylene and alpha-olefins. Such alpha-olefins will generally have 3 to 20 carbon atoms. Polymers of ethylene and one or more of these alpha-olefins are contemplated. Preferred alpha-olefins are butene-1, pentene-1, 4-methyl-1-pentene, hexene-1, octene-1 and decene-1. Especially preferred are butene-1, hexene-1, and octene-1.

Compared to films made from previously available ethylene homo and alpha-olefin copolymer, the present invention provides an m-E-polymer film layer that is biaxially orientable without difficulty by either of the double bubble or tenter frame processes to yield an oriented film having superior optical properties, outstanding dart drop impact resistance and puncture resistance, and a dramatically increased secant modulus. A biaxially oriented m-E-polymer film according to the present invention is a stiffer film than previously available polyethylene films, has improved clarity, and is better able to withstand the rigors that a film encounters in service. Consequently, articles made from these biaxially oriented m-E-polymer films (BO-m-E-polymer films) exhibit superior properties, which allows the ethylene based polymer films of the present invention to be designed for and used in applications for which polyethylene was previously considered unattractive.

The present invention provides various articles of manufacture, typically for packaging, and methods for making these articles. Articles contemplated by the present invention include a shrink wrap pallet film; a film for wrapping goods, packages for goods such as snacks, including potato chips and dry cereals; shrink wrap films for meats and poultry; and typical film applications such as diaper backsheets. Depending upon the film stiffness required for a particular end use application, the required stiffness (secant modulus) may be engineered into the final film product, ranging from relatively soft to relatively stiff, by control of the degree of orientation imparted to the film in one or the other, or both, of the MD and TD. The present invention provides BO-m-E-polymer films for shrink wrapping individually packaged items, with applications ranging from packaging compact discs to providing poultry bags. Some of the BO-m-E-polymer films embodying this invention are serviceable as heat shrinkable packages in which a product is inserted, air is normally evacuated, the open end of the bag is closed, such as by heat sealing, and heat is applied to shrink the film for a tight and conforming fit around the product.

In other service applications wherein heat shrinkability of a film is either not desired or is an inconsequential property that will not be employed in the use of the film -- services such as liners for cereal box packaging, snack food packaging, overwrapping of fresh cut produce, and the like -- by appropriate selection of m-E-polymer resin density and control of the degree of orientation imparted to the film, final film products of a desired degree of stiffness and of a desired range of vapor transmissibility to O₂, CO₂ and H₂O may be produced that are structurally strong (tensile strengths, puncture strengths, tear strengths) and of good optical properties (haze and gloss).

The end use service intended for the m-E-polymer film will in part influence the selection of the ethylene polymer resin for production of the film layer and thereafter the conditions employed

for its orientation in the MD and TD. For example, films may be intended for service as a general heat shrink wrap for non-perishable good or for perishable food goods such as meats, or the like. The intended service will then require as final properties of the film certain minimum properties with respect to (1) haze and gloss, depending upon whether user viewability of the packaged goods are or are not of a practical concern; (2) oxygen and moisture barrier moderating properties, a particular concern with respect to food packaging; (3) secant modulus (flexibility - resistance to deformation), to be geared to the preference of the end user market; (4) degree of shrinkability, to be geared to the preference of the end user market; (5) puncture resistance, tensile impact, tear strengths and elongation properties of suitable minimums for service. The requisite minimum service properties required of the film for use in a particular application is then imparted to the film by proper selection of the film base m-E-polymer resin and the selection of the film forming and orientation conditions.

The m-E-Polymer Resins

Catalyst for polymerization of the ethylene based polymers here concerned are comprised of a transition metal component having at least one organo ligand which contains a cyclopentadienyl anion moiety through which the organo ligand bondingly coordinates to the transition metal cation. Such catalyst systems are now commonly referred to as "metallocene" (m) catalysts and many examples of such metallocene catalyst systems have now been described in the art.

In contrast to catalyst systems theretofore known for alpha-olefin polymerization that utilize a transitional metal component not having an organo ligand having a cyclopentadienyl anion moiety, now commonly referred to as conventional or traditional Ziegler-Natta (ZN) catalysts, metallocene catalysts are essentially single cited catalysts whereas ZN catalysts are multi-sited catalysts that generally produce a polymer resin having a great diversity of polymeric species. By contrast, an ethylene-alpha-olefin copolymer produced by a metallocene catalyst is generally much more uniform with respect to the polymeric species that comprise the resulting m-E-polymer resin, particularly with respect to the disparity between the differing molecular weight fractions thereof -- as indicated by the M_w/M_n value of the m-E-polymer resins generally being ≤ 3.0 -- and with respect to the distribution of alpha-olefin comonomer between the different molecular weight fraction thereof -- as indicated by a high comonomer distribution breadth index (CDBI) value of 50% and higher. In part, by reason of the greater compositional and molecule weight distribution uniformity achieved in an ethylene based polymer produced by a metallocene catalyst, the density of the resulting m-E-polymer resins is substantially a linear function of its mole % comonomer content and the density of the m-E-polymer resin in the 0.915 to 0.965 g/cc range of interest for films of this type may be accomplished with an ethylene content of greater than 90 wt % and a comonomer

content not exceeding about 6.0 mole %, and a comonomer content preferably not exceeding about 5.0 mole %, and more preferably of or less than 3.3 mole %. Further, such densities are achieved in the m-E-polymer resin while the polymer backbone remains substantially linear; that is, such short chain branching (SCB) that occurs along the polymer backbone is due substantially only to the alpha-olefin comonomer content of the polymer. Accordingly, although the final density of the ethylene copolymer varies somewhat depending upon the carbon number of the comonomer utilized, the magnitude of this variation with C₄-C₂₀ alpha-olefin comonomers is not substantial; the requisite copolymer densities required of the m-E-polymer resin for films of this invention may readily be achieved with low contents of comonomer such as the C₃-C₈ alpha-olefins, with butene-1 and hexene-1 preferred as the comonomer by reason of their lower cost. Such m-E-polymers having these requisites have recently become commercially available from Exxon Chemical Company in Baytown, Texas and are now identified by the trademark "EXCEED."

Production of the m-E-Polymer Resins

The ethylene based polymers utilized in the present invention are preferably produced using supported or unsupported metallocene catalysts. The polymers may be produced in many types of reactors or reaction schemes, including, but not limited to, fluidized bed or stirred bed gas phase reactors, slurry or bulk liquid reactors of tank or loop type, solution, or any other process practiced for the polymerization or copolymerization of ethylene.

Specific metallocene-type catalysts are known to be useful for producing olefin polymers, and such catalysts are described in U.S. Patent No. 5,324,800. For placing catalyst systems on a supporting medium and using the resulting catalyst, see, for example, U.S. Patent No. 5,124,418. Support techniques for metallocene-type catalysts for use in the preparation of alpha-olefin polymers are described in U.S. patent 5,240,894. While catalysts used for the examples which follow were employed in a gas phase fluidized bed polymerization, catalysts for commercial use may be used in other processes including for example, slurry and solution processes. U.S. Patent Numbers 5,324,800; 5,124,418; and 5,240,894 are hereby incorporated by reference for purposes of U.S. patent practice.

In one preferred embodiment, a catalyst system comprising bis(1,3 methyl-n-butyl cyclopentadienyl)zirconium dichloride activated with methyl alumoxane (MAO) is the catalyst of choice. Such catalysts are outlined in copending U.S. Application Serial Number 08/466,587 which is included herein by reference for purposes of U.S. patent practice.

Characteristics of the m-E-Polymer Resins

The ethylene polymers of the present invention will generally have a narrow molecular weight distribution (MWD), as characterized by the ratio of weight average molecular weight (M_w) to number average molecular number (M_n), M_w/M_n . These M_w and M_n values are determined by Gel Permeation Chromatography (GPC). The MWD for the m-E-polymers of the present invention is less than or equal to 5; preferably ≤ 3.5 , more preferably ≤ 3.0 ; and most preferred ≤ 2.5 . Embodiments of these m-E-polymers will have a density in the range of from about 0.915-0.965, preferably 0.917-0.95, more preferably 0.917-0.940 and most preferably from 0.920 to 0.94 g/cc.

Resins produced by the above referenced processes and catalysts will be homopolymers or copolymers that contain greater than 90 wt % ethylene, preferably 93 wt % ethylene or greater, and may incorporate one or more alpha-olefins comonomers in the range of from about 0.01 mole percent to about 6.0 mole %, preferably 5.0 mole % or less, and most preferably no more than about 3.3 mole % comonomer. In a preferred embodiment, the comonomer ranges from about 0.1 to about 3 mole percent.

Copolymers produced from a catalyst system having a single metallocene component have a very narrow composition distribution - most of the polymer molecules will have roughly the same or comparable comonomer mole % content. Ziegler-Natta catalysts, on the other hand generally yield copolymers having considerably broader composition distribution meaning that comonomer inclusion varies widely among the polymer molecules.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI") as defined in U.S. Patent 5,382,630 which is hereby incorporated by reference. CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci. Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature all fractions are assumed to have an $M_n \geq 15,000$, where M_n is the number average molecular weight of the fraction.

Low weight fractions generally represent a trivial portion of the polymer. The remainder of this description and the appended claims maintain this convention of assuming all fractions have $M_n \geq 15,000$ in the CDBI measurement.

From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has a comonomer content within 25 % of each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993. The m-E-polymers employed in the films of this invention have CDBI's equal to or greater than 50% the range of 50-98%, usually in the range of 50-70% and most typically in the range of 55-60%.

These m-E-polymer resins have a melt index (MI) in the range of from about 0.5 to about 10, preferably in the range of from about 1.0 to 5.0, and more preferably from 1 to 4.0 dg/min. The MI range for film production of an m-E-polymer via a blown tube technique is preferably from about 0.8 to about 2.0; for cast film production the MI range of the m-E-polymer is preferably from about 0.75 to 4.0; preferably 1 to 5.0; more preferably 1 to 4. Choice of melt index for the m-E-polymer will generally be driven by the type of extrusion process and the specific equipment in use as well as the end use for films and/or subsequent use in converting operations.

Food law compliance can be an important criterion for articles made from these resins, such compliance is usually directly affected by the extractable content of an article made from a resin. Using an n-hexane reflux procedure, a standard of the U.S. Food and Drug Administration as noted in 21 C.F.R. § 177.1520, the maximum extractables level of the products of the present invention is expected to be less than about 5 wt%, preferably less than about 4 wt%, and most preferably less than about 3 wt%.

The m-E-polymers used in this invention have an I_2/I_1 or melt index ratio (MIR) less than 35, generally in the range of from about 16 to 22. DRI ranges from about 0 to 0.4, preferably from about 0 to 0.25, more preferably from 0 to 0.2, and most preferably from about 0 to 0.15. A definition of DRI and test methods for it are described in the publication ANTEC '93 Proceedings, INSITE™ Technology Polymers (ITP) - *New Rules in the Polyolefins Structure/Rheology Relationship of Ethylene α -olefin Copolymers*, New Orleans, LA, May 1993.

The EXCEED™ m-E-polymer resin product now available from Exxon Chemical Company is a metallocene catalyst produced ethylene based copolymer. The processing of an EXCEED™ resin may be performed in a manner which is similar to that of conventional LLDPE with minimal equipment conversion required. A thermoplastic film made from an EXCEED™ resin has

demonstrated a 50 percent increase in puncture resistance and a 40 percent increase in tensile strength, as compared to a conventional polyethylene film.

One grade of EXCEED™ is a copolymer of ethylene and hexene-1 and is a linear polymer and a unique type of linear low density polyethylene. This metallocene produced m-E-polymer has a narrow molecular weight distribution (M_w/M_n), typically less than 3.0 while having useful weight average molecular weights (M_w) of greater than 10,000 and less than 500,000, and a narrow range of short chain branching (SCB) of about 12 and less than 30 SCB/1000 carbon atoms. The EXCEED™ class of polyethylenes (wherein the comonomer is a C_4 - C_8 alpha-olefin) have a substantial absence of low molecular weight and high comonomer content molecules, a substantial absence of high molecular weight and low comonomer content molecules, as indicated by CDBI $\geq 50\%$; a narrow molecular weight distribution, and slightly lower melt strength than traditional linear ethylene polymers, and a slightly flatter shear rate viscosity curve.

Making A Film Layer

Blown films produced with an annular die and air cooling and cast films using a slot die and a chill-roll for cooling are both acceptable techniques for making a film layer of the m-E-polymer resin according to the present invention. Any technique may be used, provided the resulting film meets the specifications stated herein.

Additionally, various additives including pigments, plasticizers (?), tackifiers, anti-static agents, anti-fogging agents, antioxidants or other additives are also contemplated and may be included in the resins and/or films made therefrom.

Multilayered structures may be preferred in some applications. Such structures include, but are not limited to, coextruded films, and laminated films. Laminated films can include not only one or more film layers based on m-E-polymers of the present invention, but other film layers as well, including but not limited to, polyester, polyamide, polypropylene, other polyethylenes, Saran®, ethylene vinyl alcohol, and the like. Methods of lamination include extrusion lamination, adhesive lamination, heat lamination, and the like. Other materials may be laminated to final films structures of this invention, including films based on embodiments of the present invention, for instance paper, aluminum foil, paperboard, woven and non-woven materials.

Also contemplated are films where one or more layers are at least partially cross-linked by radiation. Such radiation and the techniques to achieve it are well known to those of ordinary skill in the art. These techniques include both gamma (cobalt 57) and x-ray radiation, electron beam and ultraviolet.

The film of the present invention can be any suitable thickness, depending upon the end use for the film. Typical thicknesses may range from about 3 microns to about 0.030 inches (0.25 mm) for a thin film to about 1 to 2 mm if a thick film is desired. The film can be obtained in a rollstock format for automatic form, fill and seal equipment or as preformed bags or pouches.

Making Oriented Film

The metallocene produced polyethylene films of this invention can be heat-shrinkable, that is an oriented m-E-polymer film can return to its original unstretched size when heated to its softening point. The terms "orientation" and "oriented" describe a manufacture of metallocene m-E-polymer heat shrinkable films. The m-E-polymer resin is heated to its flow or melting point and extruded through a die into either tubular (blown bubble) or sheet (cast) form and then cooled from its extrusion temperature. After cooling, the relatively thick extrudate is, as necessary, reheated to a temperature range suitable to orient or align the crystallites and/or molecules of the base m-E-polymer resin. An orientation temperature range for a given resin must be determined. The orientation temperature range is a range of temperatures in which the intermolecular configuration of the resin is revised by physical alignment of the crystallites and/or molecules of the resin to improve certain mechanical properties of the film, such as shrink tension as, for example, measured in accordance with ASTM D-2838-81.

While the m-E-polymer extrudate film layer is within the orientation temperature range, it is stretched, which changes intermolecular configuration, and then cooled while in the stretched or extended position. Cooling of the film stock while in the stretched position locks the crystallites and/or molecules of the material into a desirable configuration, providing an oriented film. Upon subsequent reheating to its softening point, as may occur during a packaging operation, forces within the film cause it to shrink essentially back to its original unstretched position. In this manner an oriented film is heat shrinkable, providing a shrink wrap film.

When the stretching force is applied in one direction, uniaxial or monoaxial orientation results. When the stretching force is applied in two directions, biaxial orientation (BO) results. In a continuous operation producing a rolled sheet of film, uniaxial orientation is typically provided by running a downstream roller at higher revolutions per minute than an immediately upstream roller, thereby stretching the film. This orients the film layer along its length in the machine direction (MD). Biaxial orientation is provided by also stretching the film layer along an axis at an angle to the uniaxial axis. Typically, biaxial orientation is provided by stretching in the machine direction and in a transverse direction (TD) at a right angle to the machine direction which is along

the width of the film layer. Transverse stretching can be provided by a machine called a TM Long or by a machine called a tenter frame stretcher.

A monoaxially oriented film typically refers to films oriented primarily in the longitudinal direction. However, some incidental orientation can be present in the transverse direction. The term can also refer to films oriented principally in the transverse direction, such as can be provided in a blown tubular film, with or without some incidental orientation in the longitudinal direction. A biaxially oriented film (BOF) for purposes of this application means a film the film layer of which, after its initial formation, is then intentionally and specifically oriented in the longitudinal direction (MD) and transverse direction (TD) by a degree that is beyond that which may be imparted a mere blown bubble process of forming the initial film layer itself; with the longitudinal direction being in the direction of the machine and transverse direction is the direction transverse to the machine. The biaxial stretching of the m-E-polymer film of the present invention can be carried out simultaneously or successively, with successive biaxial stretching being preferred, in which stretching is first carried out longitudinally then transversely. The preferred percentage of shrinkability of a film of this invention in the machine direction is 76%. This provides a film having good machinability and a wide sealing range.

Oriented m-E-polymer films may be produced by either post extruder manipulation of a blown film through heating and orientation (often called "double bubble" or "trapped bubble"), or by longitudinal stretching of an extruded sheet followed by tentering techniques. Orienting the film by a tentering technique is preferred since this generally produced a biaxially oriented film of superior mechanical/physical properties compared to orientation by a double bubble technique. Films after orientation are generally in the range of from about 0.2 to about 10 mils (5.08 to 254 μm) thick (gauge), preferably from 0.5 to 5 mils, and most preferably from 0.6 to 3 mils. Films layers formed by cast or blown bubble techniques to be produced into oriented structures will generally necessarily be thicker prior to orientation and will range from about 4 to about 25 mils. Choice of the thickness (gauge) prior to orientation will depend on orientation equipment, degree of intended orientation, and the properties intended of the film and/or resin. All such parameters are well within the skill and knowledge of those of ordinary skill in the art to determine, as a matter of routine setup, of a film line.

For purposes of this document, biaxial orientation will include orientations such as 2x2, 3x5, 5x5, 6x6, 7x7, 5x8 and the like. These notations will indicate a combination of film stretching in both the machine direction (MD) and transverse direction (TD) where 2 or 3, for instance indicate

200 or 300 percent difference in dimension after orientation. The amount of orientation need not be equal in both directions.

Film Properties

Compared to films made from previously known ethylene homopolymers copolymers or blends thereof, oriented m-E-polymer films made according to the present invention will generally be clearer, stiffer, stronger and exhibit greater shrinkage when heated. These stiffer, clearer and stronger BO-m-E-polymer-films may be used to make packages for crisp snacks, fresh meat, fresh produce, consumer soft and hard goods and the like.

Films made from the polymers of certain versions of the present invention may be used to contain food articles such as meats and snacks for instance. Such m-E-polymer so be used to protect and display articles of apparel and other consumer goods such as computer software, books, compact discs and a wide variety of magnetic storage media.

Various embodiments of the BO m-E-polymer films of the present invention have the following properties and ranges:

Haze	0 to 5, preferably 0 to 3, more preferably 0 to 2 %;
Gloss	greater than 70, preferably greater than 80, more preferably greater than 85;
Film densities	from 0.917 to 0.960 g/cm ³ ;
Dart Drop Impact	above about 400 g/mil at a resin density of 0.917g/cm ³ ;
Peak Puncture Strength	greater than 40 lbs, preferably greater than 45 lbs/mil, more preferably above about 50 lbs/mil;
Puncture Break Energy	greater than about 25, preferably greater than 30 in-lb/mil;
Oxygen transmission (OTR)	less than 600, preferably less than about 550, and more preferably less than about 500 cc-mil/100in ² -atm/24 hrs; and
Water Vapor Transmission Rate (WVTR)	less than about 1, preferably less than about 0.9, and more preferably equal to or less than about 0.8 g-mil/100 in ² -24 hrs.

With ethylene polymers of certain embodiments of this invention it will be possible to design final film properties broadly by controlling polymer properties such as density. For instance, in lower density ranges, e.g. 0.917 - 0.925, preferably 0.917 - 0.920 g/cm³, biaxially oriented (BO) m-E-polymer films will be relatively soft, but strong and with excellent clarity. These lower density

BO m-E-polymer films will compete favorably with plasticized PVC films in applications such as meat wrap. On the other end of the spectrum, at higher densities, e.g. 0.920 - 0.960, preferably 0.925 to 0.950 g/cm³, BO m-E-polymer films fabricated from these ethylene polymers will have a high modulus and be very stiff and have excellent clarity. These BO higher density m-E-polymer films will compete favorably with biaxially oriented polypropylene in either single or multiple layers in applications such as snack and cereal packaging.

For a given m-E-polymer density, the biaxially oriented films of the present invention exhibit many improved physical properties as compared to substantially unoriented films such as standard blown or cast films. In addition biaxially oriented m-E-polymer films of this invention have better optical properties, exhibiting excellent clarity. Tensile at yield for these biaxially oriented m-E-polymer films can be expected to be 120-300% (MD) or 150-600% (TD) minimum greater than tensile at yield for a substantially unoriented film.

Oriented films based on the ethylene polymers of the present invention may find applicability in retail fresh meat packaging. In such packaging the meat is often placed in a tray, frequently made of foamed polystyrene and then typically over-wrapped with a plasticized PVC film. Attempts in the past to utilize polyolefins, more specifically ethylene polymers, have centered around improving the ethylene polymer's recovery to equal or exceed that of PVC. However, oriented m-E-polymer films according to the present invention do not depend upon recovery. Instead, these oriented films are relatively unyielding and thus are unlikely to indent under normal handling. These films are resistant enough to stress to successfully resist indentation, which is exemplified by their high tensile at yield. Although these films are relatively unyielding, the films are still soft enough to allow easy wrapping and thus will compete favorably against plasticized PVC film in these applications.

Shrink Wrap Films

Film of the present invention offers improved performance in the shrink-wrap market. The film includes at least one layer comprised of a polymer of ethylene polymerized in with a metallocene catalyst in the presence of a C₃ to C₈ alpha-olefin comonomer. Preferably, the layer is selected from an ethylene alpha-olefin copolymer having a density of and above 0.917 g/cm³ wherein the comonomer is a C₄-C₈ alpha-olefin. The final film may have multiple layers, and the thickness of the layers may be reduced without changing the product quality.

Each layer of the shrink wrap film is preferably comprised of a resin manufactured using a single-site catalyst, a metallocene. The shrink wrap film is preferably comprised of a metallocene produced linear low density polyethylene (m-LLDPE) resin of density from about 0.917 to about 0.940 g/cm³ which is cast or blown to a film layer that is then oriented in the MD and TD to produce

products such as stretch film, heavy-duty shipping sacks, flexible processed-meat packaging, poultry bags and the like. A preferred use of the BO-m-LLDPE film is shrink wrapping products such as compact discs. This improved film exhibits an increase in puncture resistance and an increased tensile strength over the existing films used for shrink wrapping. Additional layers can include, as desired, a barrier or oxygen layer for shrink wrapping food products and pallets of food. If the film structure is more than one layer, the layers can be joined by any suitable means. Co-extrusion is preferred.

For purposes of this application a m-LLDPE is an ethylene-alpha-olefin random copolymer having densities preferably from about 0.917 to 0.940 g/cm³. The alpha-olefin comonomer used in m-LLDPE is usually butene-1, hexene-1 or octene-1; however, other comonomers can be used, such as 5-methyl-1-pentene, or any other C₃-C₈ alpha olefin. Branches of the preferred m-LLDPE are short chain branches, 6 carbons and less, due to the comonomer, and the m-LLDPEs do not have many long branches off the main chain. The branching of this resin controls density and crystallinity. The preferred density of the metallocene LLDPE used in the film structure of the present invention is 0.917 to 0.924 g/cm³. The shrink wrap films of the present invention comprised of such m-LLDPE exhibit improved haze and gloss.

The metallocene LLDPE biaxially oriented film of the present invention meets the requirements of the shrink wrap industry by having excellent stretch and resistance to deformation and being resistant to abrasion. Thus, the film of the present invention has good machinability, adequate slip properties and is resistant to burn through.

For the shrink-wrap market, biaxially oriented films made according to the present invention offer superior properties. The biaxially oriented films shrink more, and this property, combined with other desirable properties, makes these BO-m-LLDPE films desirable for the shrink-wrap market.

Higher Density BO-m-E-Polymer Films

Films of the present invention may also comprises a biaxially-oriented high density polyethylene (HDPE) based on a metallocene or single-site catalyst (m-HDPE). The preferred density of the metallocene HDPE used in this film structure of the present invention is 0.925 to 0.960 g/cm³. This film exhibits greater impact strength, improved puncture resistance, and improved optics in haze and gloss as compared to a traditional ZN-HDPE.

The biaxially oriented film of the present invention has at least one layer comprised of m-HDPE that can be used as a replacement for certain applications involving polypropylene or nylon. A m-HDPE film can be used as a barrier layer in multilayer films for packaging or for skin packaging films. The m-HDPE film of the present invention has a high molecular weight and is

extrusion blown, and as biaxially oriented it can be used to produce clear shopping bags for use in a retail application. This BO-m-HDPE film can also replace polyethylene-nylon structures for uses as containers for food, medicine and the like.

A m-HDPE film can preferably undergo a blown film extrusion process with at least one additional film layer. The resulting film is a thin gauge, single or multilayer m-HDPE film with good heat seal performance, excellent strength and uniform thickness or roll quality.

Industrial applicability

Films according to the present invention are especially useful for packaging individually wrapped items, for instance, musical compact discs, software computer packages, musical tapes, and pallets of bulk items. However, the invention is not necessarily limited by the product contained within a package made from the inventive film as the film can suitably be used whenever a "wrapping" is desired, such as for winterizing windows from the influx of cold air.

Furthermore, the inventive film and packages therefrom exhibit excellent clarity and seal strength. Thus, the inventive film and packages are suitable for the food service industry (e.g., hospitals, schools, restaurants, fast food, etc.) and the shrink wrapping industry (e.g., stretch film used in the retail music business, computer software business, toy business, and the construction business) where appearance and seal strength are especially important and long shelf-life may be required.

Numerous applications are contemplated for these biaxially oriented m-E-polymer films of the present invention. The high clarity, variable stiffness, and the engineerable oxygen (OTR) and water vapor transmission rates (WVTR) make these films highly advantageous in applications such as modified-atmosphere packaging for fresh fruits, vegetables, meats and the like. These biaxially oriented m-E polymer films conform to the contours of products very well as compared to, for instance, oriented polypropylene. Thus, these biaxially oriented m-E polymer films are desirable as label stock (pressure sensitive, adhesive and the like).

These biaxially oriented m-E polymer films can have a relatively high one-percent secant modulus, which means that these films can be relatively stiff. Further, these films have a relatively low water vapor transfer rate (WVTR), which is good for keeping dry foods dry and moist foods moist. The stiffness of these BO-m-E polymer films conveys a sense of crispness, making these films desirable for packaging dry snacks such as cookies, crackers, potato chips, corn chips, peanuts, pretzels and the like, while the low WVTR keeps the snacks dry and crisp. Similarly, these films are well suited for applications including cereal packaging as an inside liner/container, particularly

since these films can be heat sealed. For such applications either single or multilayer films and/or bags can be used.

The high percentage shrink and the low oxygen transfer rate (OTR) makes the biaxially oriented m-E-polymer films particularly well suited for shrink-wrap packaging of fresh, cooked, and processed meats, poultry, fish, and the like, as well as other moist foods subject to spoilage.

These films can be metallized for packaging of foods and for decorative applications, and/or they can be made opaque for packaging, for instance, candy bars. On the other hand there are numerous nonpackaging applications for which these films are suitable such as for document or photo protective covers.

The package formed from the film structure of the present invention can also contain resealing means positioned away from a peripheral heat seal. For instance, a slot means can be provided on one interior face and tab means on an opposing interior face of the package such that after the heat seal is cut away, a consumer can reseal the package by pressing the tab into mating engagement with the slot. Such resealing means or slot and tab means are existing in the art.

Printing can be applied directly to the film if desired and ink can be imparted to the film by a flexographic or rotogravure apparatus. For food packaging the ink employed must be suitable for the application. The printing can be placed upon an outer or inner exposed surface or upon an inner surface of a multilayer film.

To make a package easier to open, a tear line can be provided. The film can be laser scored to form a single line or parallel lines of weakness in at least one layer of film of the present invention by partially vaporizing the film with a beam of radiant energy. The score lines form a tear path in a multilayer film. When the film is formed in a package, the score line may extend across the entire surface of the film.

EXAMPLES

A series of films were made and subsequently oriented by a tenter frame process. The properties of both oriented and non-oriented films (UO) were compared. To further demonstrate the differences, comparisons to commercial clear films were also included.

Definitions and Test Protocols

For the purposes of this application, parameters and tests referenced herein are defined as provided in Table 1. A procedure for measuring shrinkage is provided below.

Table 1.

<u>Property</u>	<u>Units</u>	<u>Definition or Test</u>
Density (d)	g/cm ³	ASTM D-792
CDBI	%	described within
Melt Index (MI)	dg/min	ASTM-1238(E)
Molecular weight distribution (MWD)	none	GPC
I ₁ /I ₂ (MIR)	none	ASTM D-1238
Haze	%	ASTM D-1003
Gloss	%	ASTM D-2457
Dart Drop Impact F ₅₀	g/mil	ASTM D-1709
Puncture (peak and break energy)	lb and in-lb/mil	Exxon Method
Oxygen Transmission Rate (OTR)	cm ³ -mil/100 in ² atm. /24 hrs @ 25°C	Exxon Method
Water Vapor Transmission Rate (WVTR)	g-mil/100 in ² /day @ 38°C	(ASTM E96)
Tensile at Yield	K psi	ASTM D-882
Elongation at Yield	%	ASTM D-882
Ultimate Tensile (at Break)	K psi	ASTM D-882
Elongation at Break	%	ASTM D-882
Secant Modulus (1%)	K psi	ASTM D-882
Elmendorf Tear	g/mil	ASTM D-1922
Shrinkage	%	Described below

To measure shrinkage, condition a sample at $23 \pm 2^\circ \text{C}$ and $50 \pm 5\%$ relative humidity for at least 16 hours prior to testing and 40 hours following fabrication. From a clean, wrinkle-free portion of the film sample, cut three to five circular specimens using a 100 mm circular die. The specimens should be representative of the entire film width. Draw a line on each specimen indicating machine direction (MD).

Rub a small amount of talc on a heat resistant tile and preheat the tile for uniform test results. Place a film specimen on the preheated tile using tweezers. Center a heat gun one to two inches over the sample and turn on the heat gun for about 45 seconds. Shrinkage will begin immediately, and ultimate shrinkage occurs after about 10-45 seconds depending on film thickness. Cool the sample with air. Repeat this procedure for each specimen. Measure each specimen along the line indicating the machine direction and subtract the length in mm from 100 mm to yield a percent shrinkage in

the machine direction. To determine a percent shrinkage in a transverse direction, repeat the measurements along a transverse axis.

Example 1

Exceed® 301 (now EXCEED® 357C32), an ethylene copolymer with hexene-1 manufactured with a metallocene catalyst by Exxon Chemical Co., Baytown, Texas, having a 0.917 g/cm³ density, a 3.4 melt index and having a peak melting point of 115°C (by DSC), was cast into a 15 mil film on a Killion extruder. Subsequently, the film was placed in a T.M. Long film stretch laboratory tenter frame orientation device and oriented to 5x5, indicating the amount of orientation or stretch in the machine direction (MD) and transverse direction (TD), respectively. The stretcher was manufactured by T.M. Long of 405 Bridge Street, Summerville, NJ 07986. Orientation temperatures used were 235, 245 and 250°F. These BO-m-E-polymer films, by comparison to an unoriented film cast (cast-UO) of the same m-E-polymer (EXCEED 301) to a gauge comparable to that obtained in the BO-m-E-polymer films, had nearly comparable haze and gloss properties as the cast film but otherwise the physical strength properties (tensile and secant modulus) of the BO-m-E-polymer films were dramatically improved. The tensile at yield (TD) improved by 200 to 300%, and the secant modulus improved by 150 to 200% (MD or TD). Tensile at yield, elongation at yield, and ultimate tensile all were improved by the orientation, while Elmendorf tear, as may have been expected, worsened with orientation. As compared to blown films of EXCEED® 301 this biaxial orientation improved clarity, tensile at yield, and secant modulus.

Example 2

A film sample from EDC 103 (now EXCEED® 350D60), an ethylene-hexene copolymer of density 0.917 g/cm³, 1.0 melt index, 17.2 melt index ratio, CDBI about 58, MWD about 2.3, and peak melting point 118°C (by DSC) manufactured by Exxon Chemical Co., Baytown, Texas, was made to a gauge of 1.62 mil and a 5 x 8 biaxial orientation. Two films of the EXCEED 350 D60 resin were also made by a blown bubble process, one to a greater gauge (3 mil) and the other to a lower gauge (0.8) than that of the oriented film and these blown films (blown-UO) were not thereafter oriented. Fig. 1 is a radar plot that compares the final film properties measured for the BO Em-E-polymerfilm and the unoriented blown m-E-polymer film of 0.8 mil gauge.

Example 3

A biaxially oriented polypropylene (BOPP) film commercially available as Bicolor® B from Mobil Chemical Co., Beaumont, Texas, and is believed to be based on a homopolymer polypropylene is compared in its properties with respect to a 5 x 8 biaxially oriented film of EDC 103 (or EXCEED 350 D60) at 1.62 mil gauge vs. Bicolor B® at 1.25 mil in Figure 2. Compared to

the oriented film prepared from EDC 103, an ethylene-hexene copolymer of 3 mole % hexene, $d = 0.917 \text{ g/cm}^3$, $MI = 1$ prepared from a metallocene catalyst, the BO EDC 103 film, by comparison to the BOPP film, exhibited reduced haze and 1 % secant modulus; comparable tensile strength and WVTR, greater Elmendorf tear strength and OTR.

Example 4

Two film samples, Exceed® 377X600, an ethylene copolymer with hexene-1, having a 0.922 g/cm^3 density and Exceed® 399X60, an ethylene copolymer with hexene-1, having a 0.926 g/cm^3 density, were biaxially oriented to a 6 x 6 degree using a T.M. Long stretcher. For the Exceed® 377X 60 sample, haze improved from 17.7 for an unoriented blown film to 1.1 % for a biaxially oriented film, while for the Exceed®, 399 x 60 sample, haze improved from 13.8 to 2.9 % compared to its blown film analogue. The biaxial orientation caused both orient films to become much stiffer, as indicated by a higher one-percent secant modulus. For both film samples the tensile strength at yield and the ultimate tensile strength increased significantly with orientation.

Example 5

Exceed®301 (now EXCEED 357 C 32) , an ethylene-hexene copolymer of 3 mole % hexene, density 0.917 g/cm^3 , melt index of 3.4 was processed by the procedure of Example 1 into a 5 x 5 biaxially oriented film and its mechanical/physical/chemical properties were determined, including its WVTR. A film of comparable WVTR comprising a HDPE ($d = 0.96 \text{ g/cm}^3$) prepared by a blown bubble procedure (and commercially available from Exxon and employed for various services) -- such as is the case for preparing cereal box liner films of an HDPE -- and the properties of the blown HDPE film were determined. Figure 3 presents a comparison of the properties of the respective films wherein between the two film samples the highest value of a film property is assigned as 100% and the value of that property in the other film is plotted as a percentage of that highest film property value. Accordingly, as shown by Figure 3, the WVTR value of each film is 100%. The biaxially oriented Exceed® 301 film had the greatest dart impact and Elmendorf tear resistance (the HDPE film being of less than 15% of these values) and the least haze (plotted as 1/HAZE). The HDPE film had the greatest secant modulus, with the biaxially oriented Exceed® 301 film having about 35 % of the secant modulus of the HDPE film. The comparison establishes that a biaxially oriented m-E-polymer film of this invention would be a ready and desirable replacement film for HDPE films now made for service as cereal box liner films.

Example 6

EXCEED polymers of three differing densities; namely EXCEED 350 D60 of density 0.917 g/cm^3 , EXCEED 377 X 60 of density 0.922 g/cm^3 and EXCEED 399 X 60 of density 0.926 g/cm^3 ;

were produced as biaxially oriented films wherein the EXCEED 350 D60 was 5 x 8 oriented and the other films were 6 x 6 oriented films. Radar plot Fig. 4 illustrates the relative differences in the properties for these films.

Table 2 hereafter identifies the resin and film properties respecting all cast, blown and biaxially oriented films that were prepared and reported by these Examples 1-6.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, films, especially oriented films, have been exemplified in the present application. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred version contained herein.

CLAIMS

We claim:

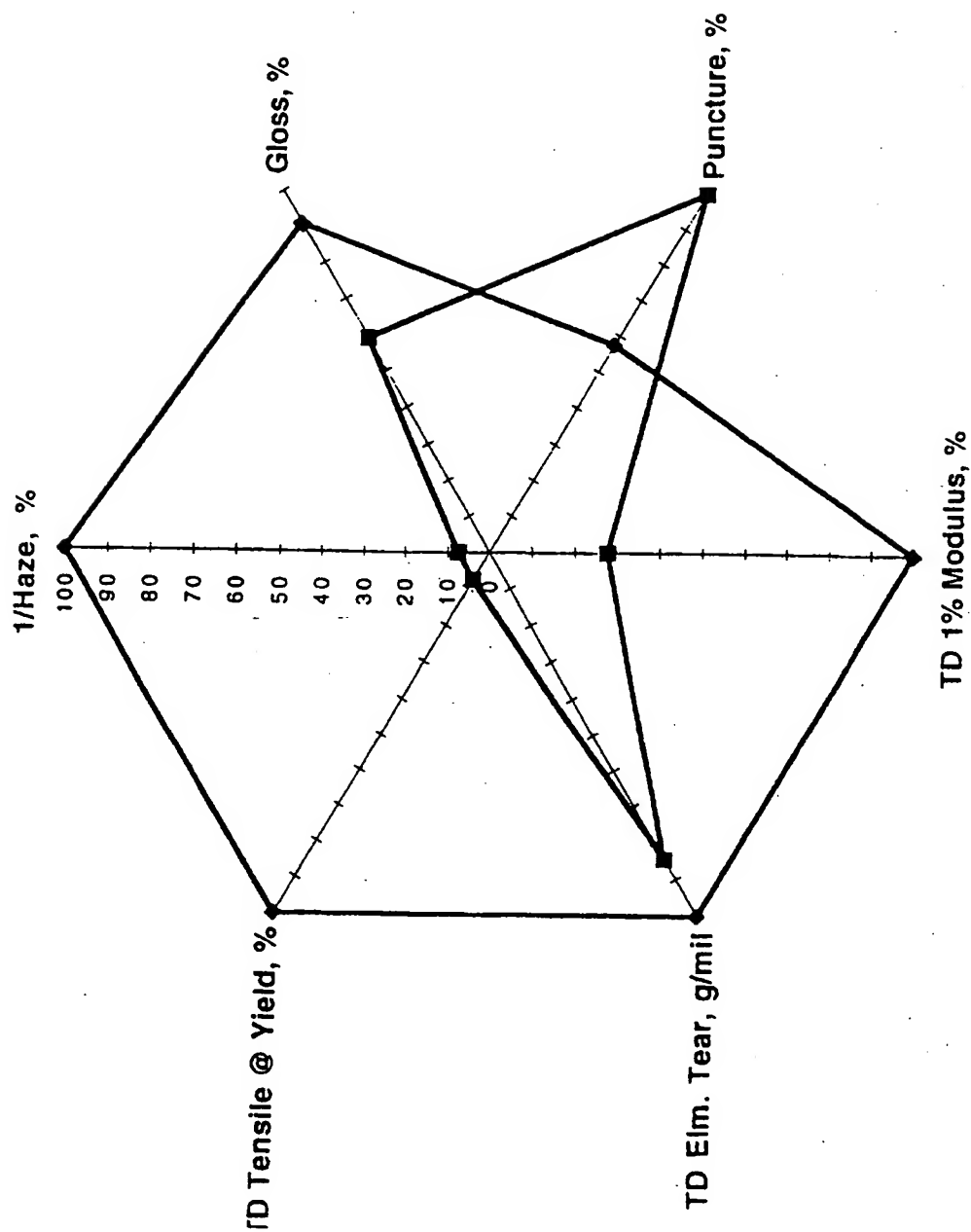
1. A film, comprising; a biaxially oriented film layer composed of a thermoplastic ethylene polymer having an ethylene content of greater than 90 wt%, a CDBI greater than 50%, a content of 0 to 6.0 mole % of a C₃-C₂₀ alpha-olefin comonomer and a density of 0.915 g/cc or greater.
2. A film, comprising; a biaxially oriented film layer which comprises a thermoplastic consisting of an ethylene polymer having an ethylene content of greater than 90 wt %, a CDBI greater than 50%, a content of 0 to 6.0 mole % of a C₃-C₂₀ alpha-olefin comonomer and a density of 0.915 g/cc or greater.
3. A film, comprising; a biaxially oriented film layer composed of a metallocene catalyzed ethylene polymer having an ethylene content of 90 wt % or greater, a density of from about 0.917 to about 0.95 g/cm³, a CDBI greater than about 50%, a content of 0.01 to 5.0 mole % of a C₄-C₈ comonomer.
4. The biaxially oriented film of claim 1, wherein said ethylene polymer has a M_w/M_n less than about 3, and a M_z/M_w less than about 2.
5. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized using a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a secant modulus of at least 25,000 psi.
6. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a haze less than 5 %.
7. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer having a tensile strength at yield greater than 1,800 psi.

8. A film, comprising; at least one biaxially oriented film layer of polyethylene polymerized from a metallocene catalyst system, said polyethylene having a density of at least 0.917 g/cm³, and said film layer shrinking at least 40 % when heated to a softening point.

9. A film, comprising; a biaxially oriented film layer formed of a thermoplastic ethylene polymer resin having an ethylene content of greater than 90 wt %, a CDBI greater than 50 %, a content of 0 to 6.0 mole % of a C₃-C₂₀ alpha-olefin comonomer and a resin density of at least 0.915 g/cm³, wherein density of the biaxially oriented film layer is greater than the density of the resin from which said film layer was formed.

FIGURE 1

Biaxially Oriented v Blown Exceed
0.917/1MI; 350D60

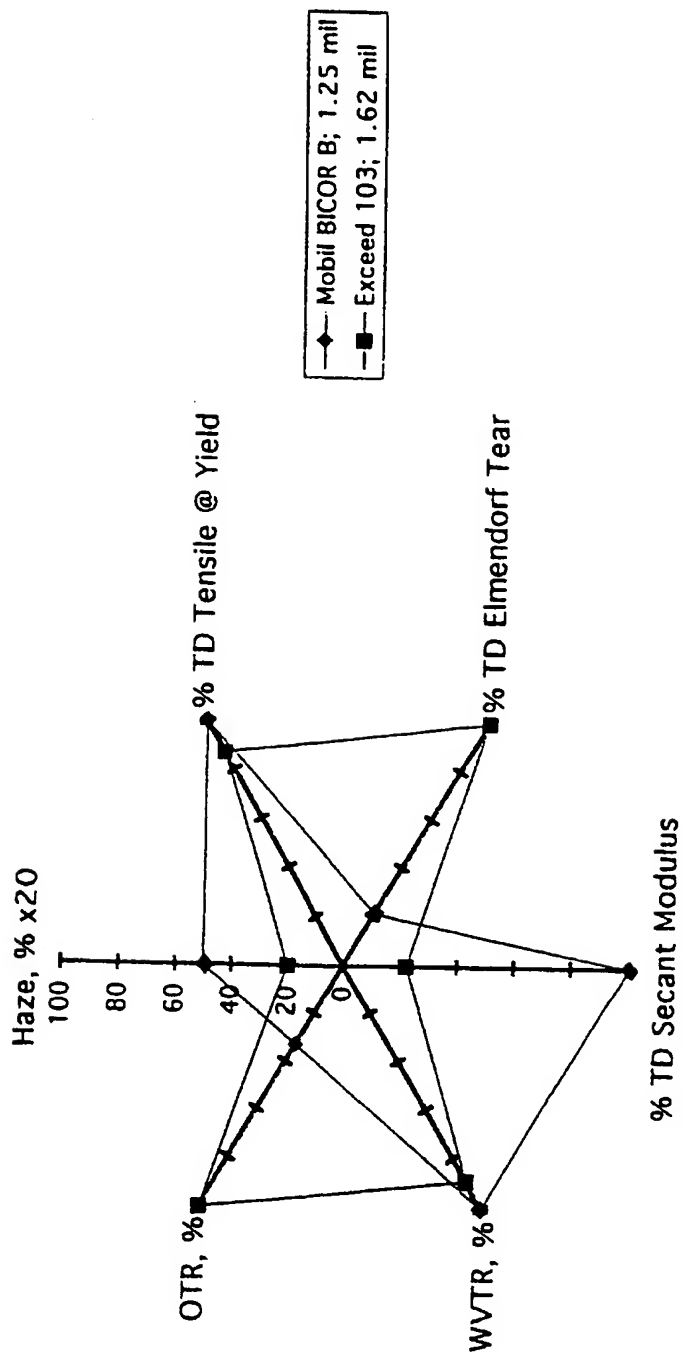


1/4

2/4

FIGURE 2

Properties Comparison: Biaxially Oriented Exceed v Polypropylene



3/4

FIGURE 3

Properties Comparison: Cereal Liner Application

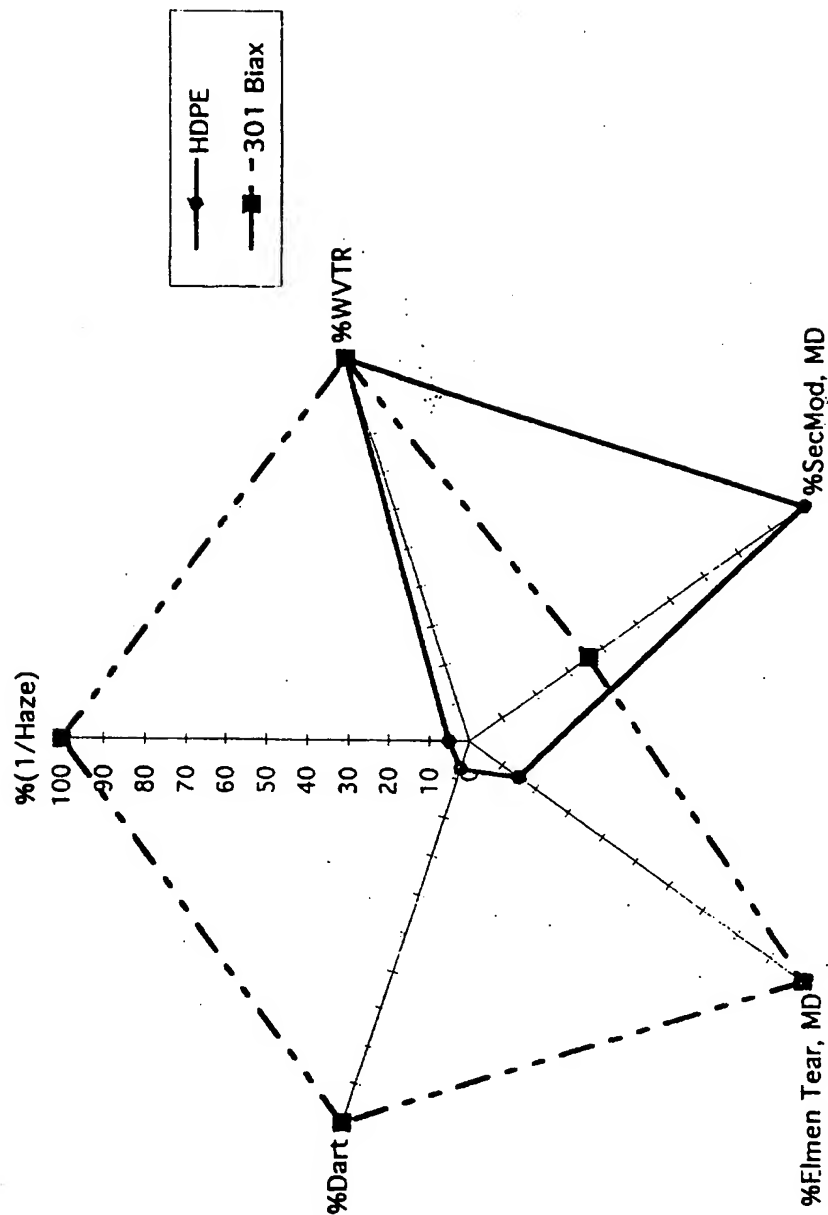
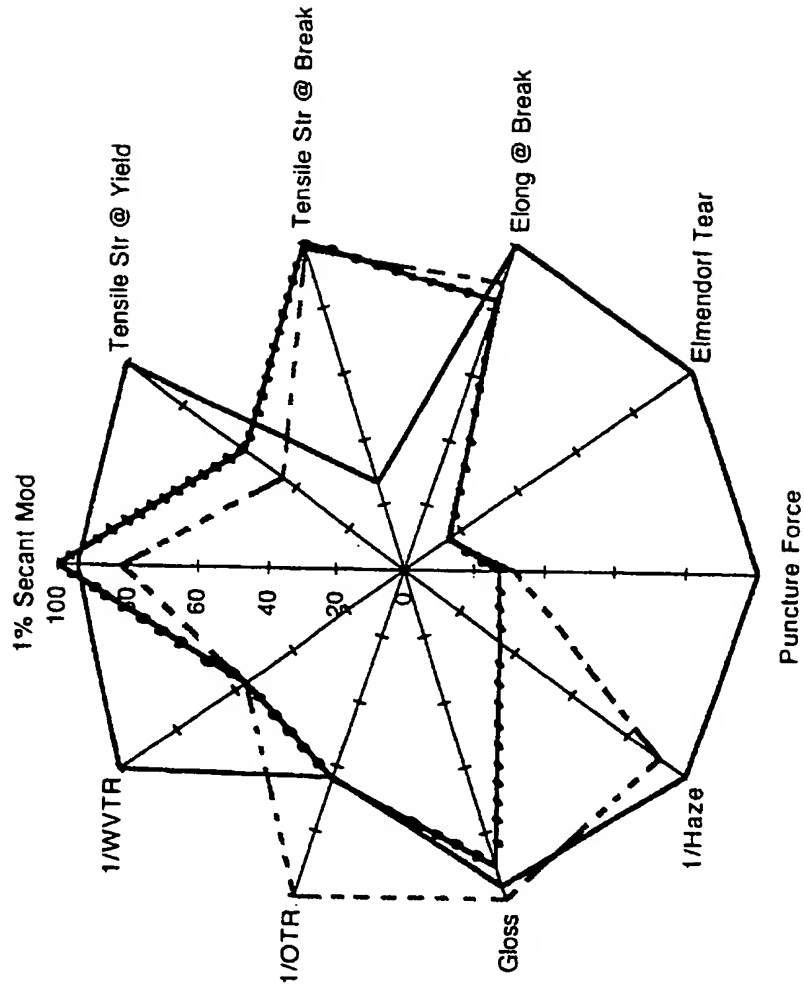


FIGURE 4

Properties Comparison for Biaxially Oriented Exceeds



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20180

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,397,640 A (GEORGELOS et al.) 14 March 1995, see entire document.	1-9
X, P	US 5,562,958 A (WALTON et al.) 08 October 1996, see entire document.	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:	
A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

03 MARCH 1997

Date of mailing of the international search report

18 MAR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/20180

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B32B 7/12

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

428/349, 516

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

428/349, 516

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, JPOABS, EPOABS

search terms: polyethylene, oriented, metallocene

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